Applied Optics

November
1963

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Applied Optics

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Earle K. Plyler, Feature Editor

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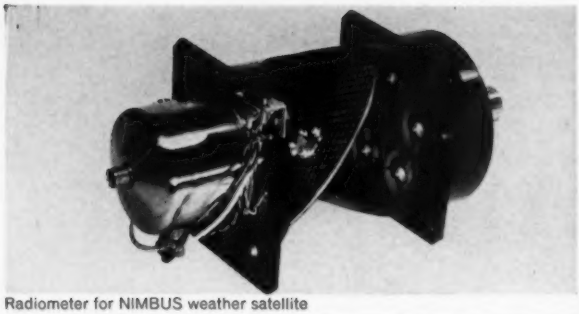
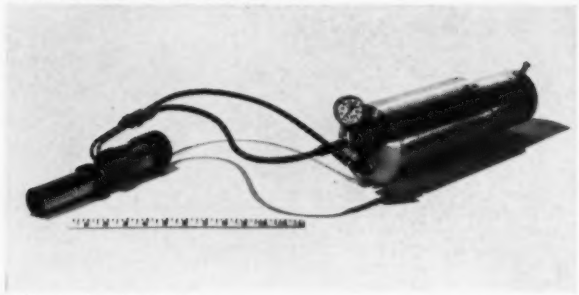


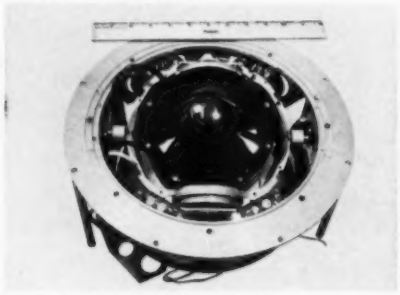
Radiometer for NIMBUS weather satellite

Interceptor IR installation



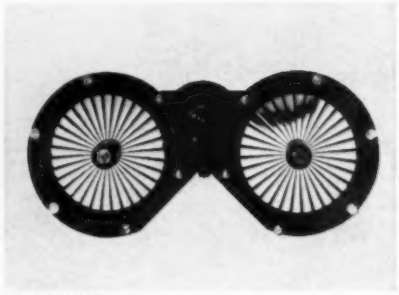
12°K closed-cycle cryostat

90C IR search/track set

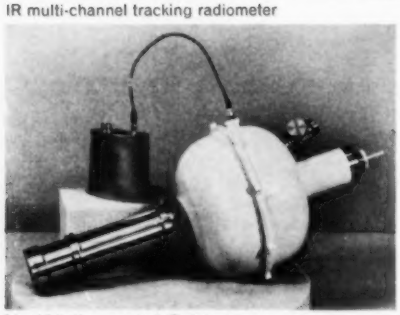


IR multi-channel tracking radiometer

Star tracker for SURVEYOR spacecraft



Modulated IR source



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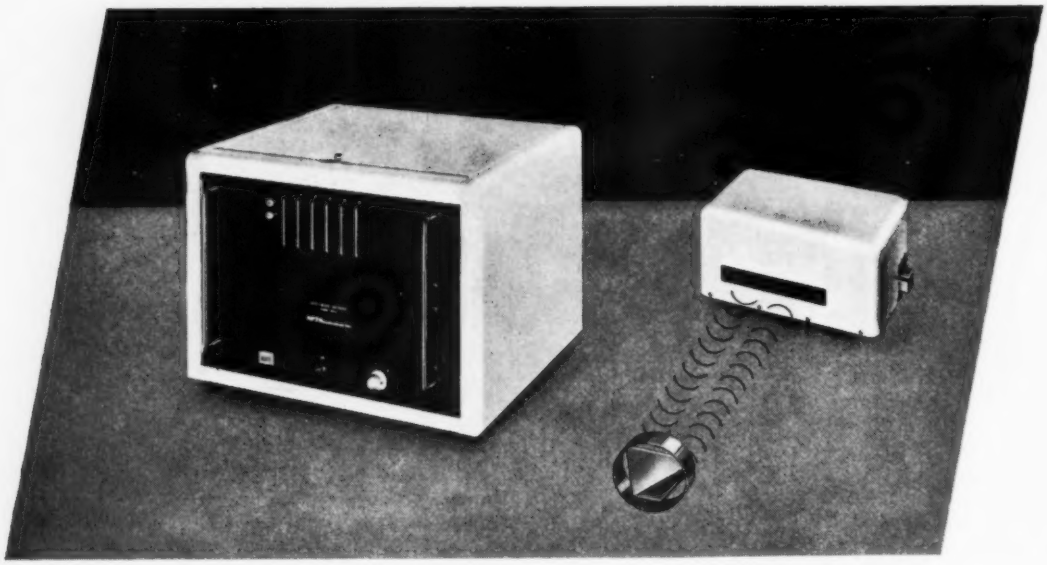

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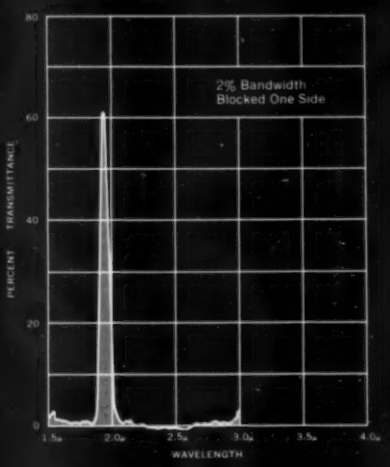

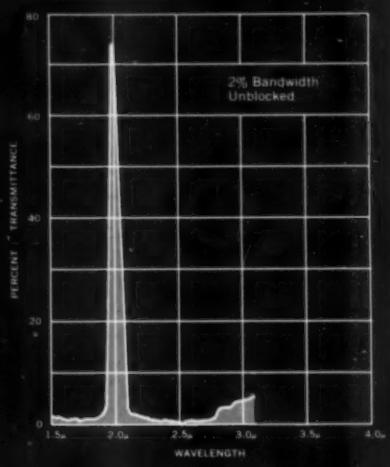

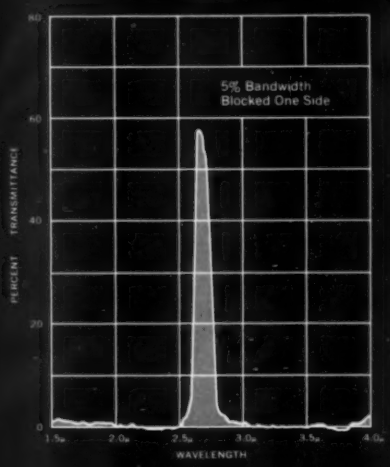

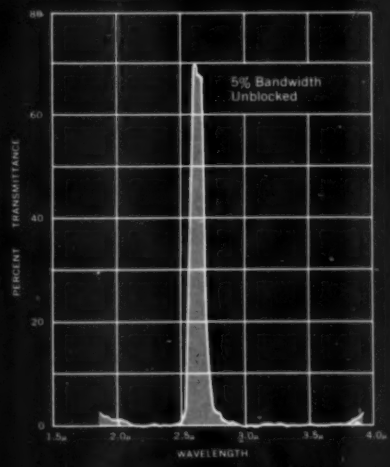

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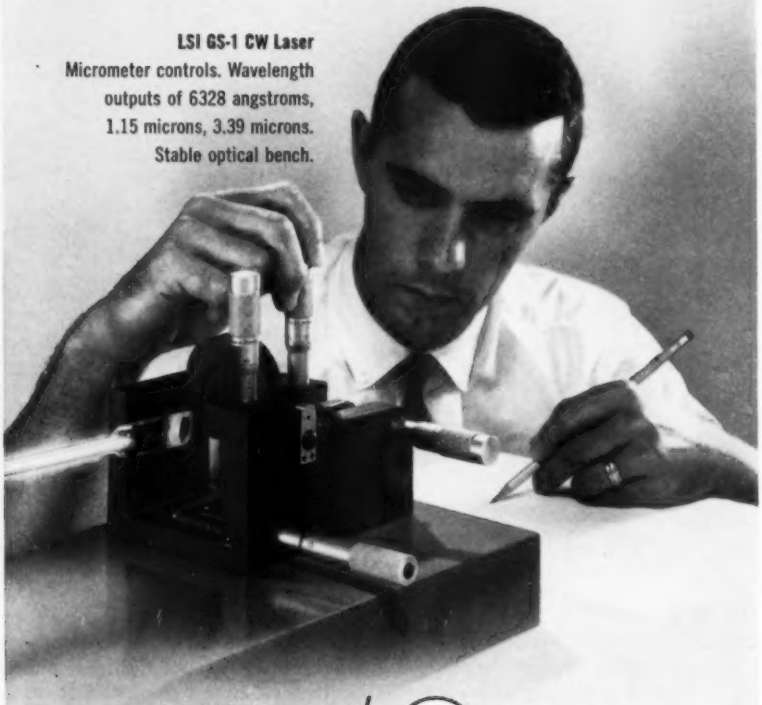

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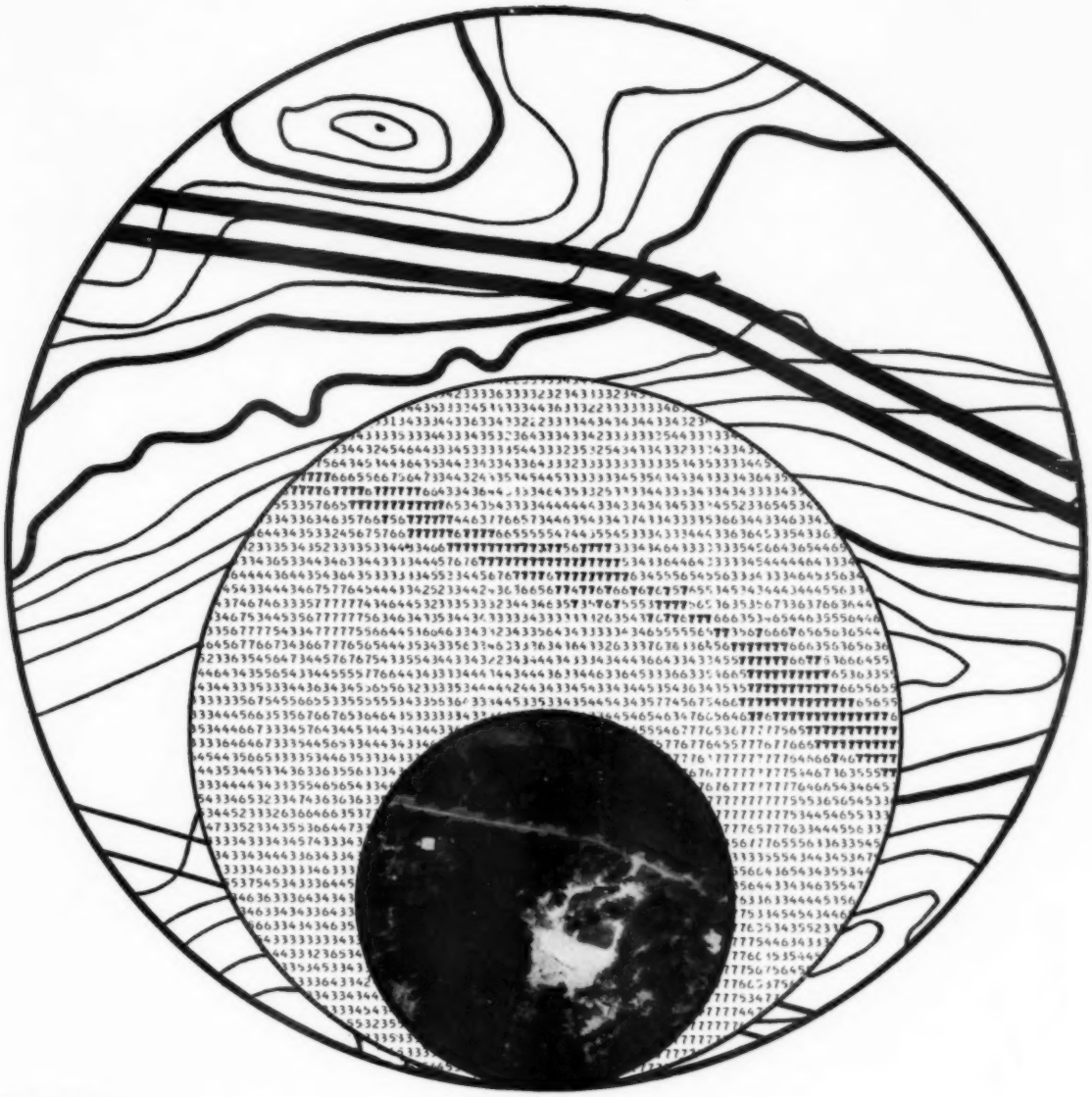

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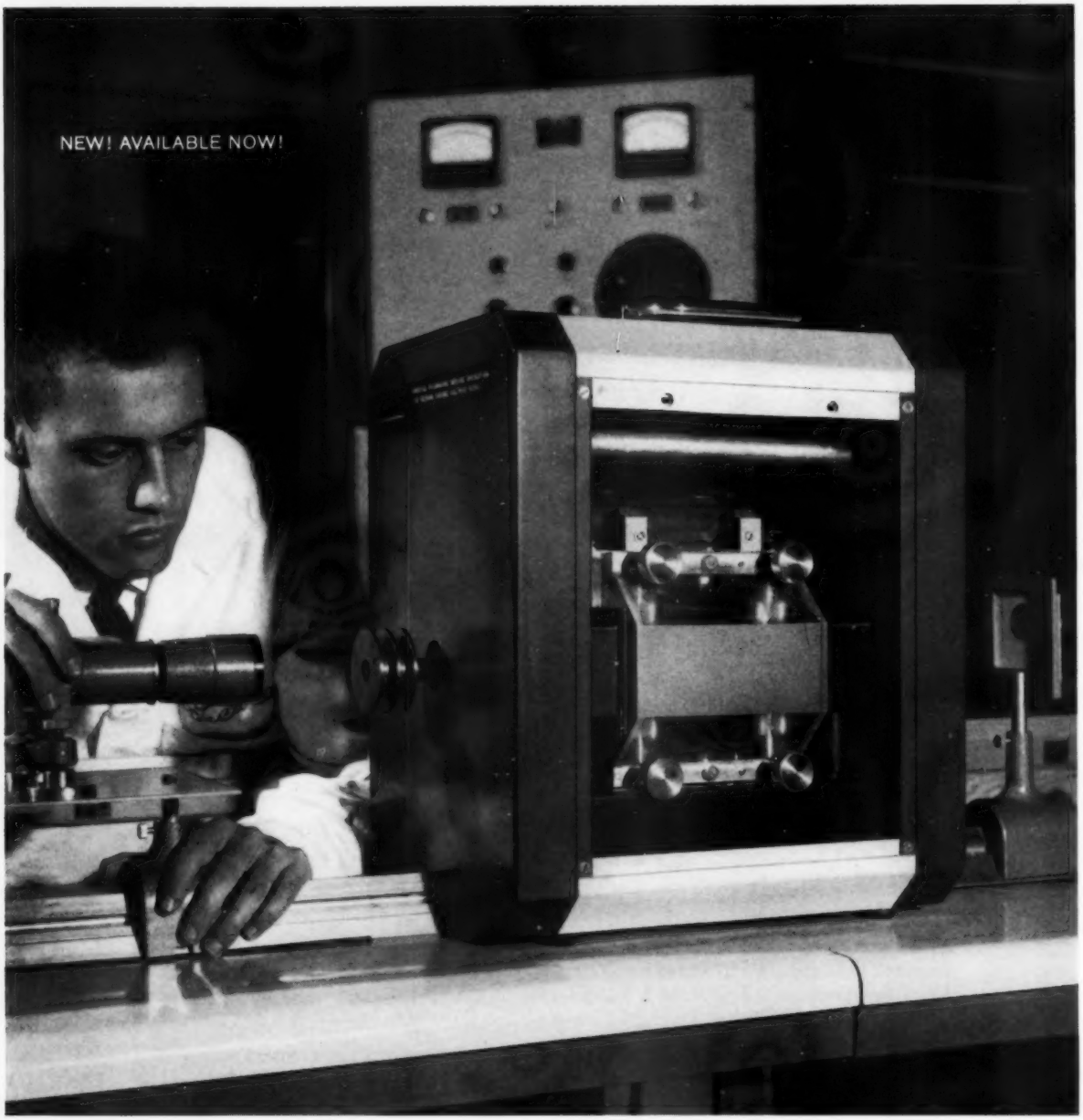

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spectroscopy

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CONFERENCE ON INTERFERENCE AND COHERENCE
Sydney, Australia, 24—25 August 1964

Provisional Subjects to be covered at a short ICO-AAS Conference on Interference and Coherence to be held preceding the conference in Tokyo and Kyoto (1–8 September 1964) include applications of interferometry to length standards and measurements, testing of optical systems, studies of the properties of materials, and to radio astronomy; new techniques in interferometry and new types of interferometers; and coherence and correlations. Both invited lectures and short papers on these topics are planned.

Provisional Timetable: Reunions at private homes on 23 August; conference sessions in Sydney University on 24 and 25 August; visits to National Standards and Radiophysics Laboratories, Sydney University, and University of New South Wales on 26 August; visits to scientific installations outside Sydney 27–29 August either as tours or by private arrangement made at the conference. OSA's Around-the-World Group Flight provides transport to this and the Tokyo meeting.

Scientific Tours could include visits to Narrabri, a country town 565 km north of Sydney, where there is an intensity interferometer for measuring stellar diameters and a radioheliograph for mapping the sun; Parkes, a country town 400 km west of Sydney and the site of a large radio telescope; Canberra, the national capital, 320 km south of Sydney (enroute to Melbourne) and the home of the Australian National University and Mount Stromlo Observatory; and Melbourne, capital of State of Victoria, the location of CSIRO Division of Physical Chemistry, the University of Melbourne, and Monash University.

Accommodations can be arranged at one of the University Colleges either for the conference only or for the full week at £A2.12.6 ($7.00) a day including meals.

Registration fee will be £A4 ($9.00) including the conference dinner. Students may register for the meeting only for £A1 ($2.20). Tours will be extra.

Additional Information can be obtained from the Australian National Committee for Optics, W. H. Steel, Convenor, CSIRO Division of Physics, City Road, Chippendale, N.S.W., Australia.

International Commission for Optics——————————————————**See page A13**

CONFERENCE ON PHOTOGRAPHIC AND SPECTROSCOPIC OPTICS
Tokyo and Kyoto 1–8 September 1964

arranged by

SCIENCE COUNCIL OF JAPAN and JAPANESE SOCIETY OF APPLIED PHYSICS

A Conference on Photographic and Spectroscopic Optics, arranged on an international level by the Science Council of Japan and the Japanese Society of Applied Physics under the auspices of the International Commission for Optics, will be held in Tokyo and Kyoto, Japan, 1–8 September 1964. The Conference will be composed of some 10 sessions, and each session will include one or two invited papers (30–40 min presentation time) and some contributed papers (15 min each). The subjects to be dealt with at the Conference will be:

Design and Evaluation of Photographic and Spectroscopic Optical Systems
Recent Instrumentation in the Far Infrared and the Extreme Ultraviolet
Optical Materials for Use in Photographic and Spectroscopic Optics

Offers of papers should be made no later than 31 January 1964, by sending an abstract to the Organizing Committee. This abstract must be adequate for the Committee to decide on the suitability of the paper: the scope of the paper should be indicated, and principal new results included. The working languages of the Conference will be English, French, and German. However, in view of the fact that English will be the only language comprehensible to the majority of participants, speakers are strongly recommended to read their papers in English.

Visits to research institutes, universities, and optical companies are being planned. More detailed information will be circulated in due course.

All inquiries concerning the Conference should be addressed to: Prof. H. Kubota, Secretary, Organizing Committee, ICO-Tokyo & Kyoto, Science Council of Japan, Ueno Park, Tokyo. For planning purposes the Japanese Committee is very eager to estimate the number of people who will attend; If you are interested in this meeting please write immediately to Prof. Kubota for further information.

WILLIAM WEBER COBLENTZ

Earle K. Plyler

The November issue of this journal was originally planned to honor Dr. Coblentz on his ninetieth birthday. Since he passed away on 15 September 1962 it is now being issued as a commemorative volume.

As a scientist and research physicist Coblentz' reputation extends throughout the scientific world, but the human side of the man was known to only a few, and if he had not written a story of his life (*Forty Years As a Researcher*) very meager knowledge of him would be available. It is somewhat surprising that a man who had frequent periods of poor health accomplished so much. He was troubled with tuberculosis most of his life and at the time of his death had an active case. Also, he had digestive disorders which became so bad at the time of his retirement that he needed to go on a very strict diet, both as to type and amount of the foods which were allowed. He followed the diet with great care, even weighing the amount of the different foods for his meals.

Dr. Coblentz had a great interest in the education of young men of high potential who needed financial assistance. He started a scholarship fund at Case Institute of Technology by giving them the gold medals which he had been awarded and later increased the fund by gifts from time to time. He no doubt remembered the difficult time he had had in financing his education and wanted to make it easier for others. He had a great feeling of gratitude to those who helped him. One lady who had helped him in his youth became ill in her later life. Dr. Coblentz brought her to Washington and paid for her care and medical expenses, besides giving her much personal attention in his spare time.

When a visitor came to Dr. Coblentz' laboratory, he was received with some reserve. On one occasion a scientist asked Dr. Coblentz if he could see his laboratory. Coblentz replied that if people continued to interrupt his work that he would never get anything done. The scientist expressed his regret and started to leave, but Coblentz called him back and said, "Since you have already stopped me I may just as well show you around". After several hours the visitor tried to leave, but Coblentz said, "Can't you stay longer? We do not close for two hours". After he retired several of his colleagues would call him about visiting in his home. He would usually reply that he was very busy and did not know whether or not he could spare the time. Then he would add that he might be able to see him for a few minutes. When the visitor arrived the idea of time was forgotten. These incidents showed that Coblentz considered work as the most important part of his daily life, but when the situation was thrust upon him he thoroughly enjoyed people.

Many present-day scientists know of the very valuable contributions which Coblentz made in many fields of science. One of the best summaries of his accomplishments is the citation which was made when he received the Frederic Ives Medal of the Optical Society of America in 1946. It is as follows:

> Dr. Coblentz's work has been so important and so voluminous that there is not time to mention more than a few of the outstanding accomplishments.
>
> The frequency with which his results are used in radiometry and photometry, and the great confidence which all physicists have in him, testified to his thoroughness and accuracy. It can be said that he established beyond a shadow of a doubt the validity of Planck's law; that the standards of radiation used in this country during the last thirty years have been maintained under his supervision; that modern radiometry from the far infrared to the extreme ultraviolet is more the creation of one man, Coblentz, than any other equally important branch of physics; and that his 1918 data on the brightness sensitivity of the human eye were among the most important data used in the determination of the standard luminosity curve adopted by the I.C.I. in 1924. These data are still standard today.
>
> Dr. Coblentz is nearly unique, as a physicist who for thirty or more years has stuck to one difficult and important program of research, radiometry, without being diverted by scientific fads.

Of the papers in this issue dedicated to the memory of Dr. Coblentz, three are contributions concerning the importance of his work. In these, three points stand out: (1) the large amount of work which Coblentz completed, (2) the thoroughness and accuracy of his work, and (3) the vision and pioneering spirit of his researches.

The career and works of Coblentz have been an inspiration and help to many scientists, and it is fitting that we should pay tribute to him by this special issue.

Coblentz' Contribution to Infrared Spectroscopy

R. Norman Jones

Ithaca in late September is beautiful, and the fall of 1903 was no exception. The lake shore foliage was shot with color, and up the hillsides whole trees were red, some outlined sharply against the blue sky. Groups of returning students ambled up to the campus from the town; through the murmur of their voices came the distant whistle of the steamboat, signaling its departure on a leisurely journey up Lake Cayuga.

This Cornell scene was lost to "Andy" Coblentz, closeted in the basement of Franklin Hall in a little room beside the storage batteries. At his back a stone pier partly hid the spectrometer he had recently built. Its use in the study of iodine films had earned him his doctor's degree. Now, three months later, he was back at Cornell as a Carnegie Research Associate and an Honorary Fellow of the University. He planned to continue work on infrared spectra and had decided to investigate organic compounds. His immediate problem was financial, not scientific. The compounds available were few; some could be had from the university museum, and Professor Mabery would lend him hydrocarbons from Case Institute, but more would be needed if the job was to be well done. Eimer and Amend listed many fascinating substances in the catalog at hand, but funds must come from his own pocket and only $54 could be spared. Decisions had to be made—could he or could he not afford $5 for a gram of stearic acid?

It is not difficult to reconstruct this picture of Coblentz at the beginning of his studies on the infrared spectra of organic compounds[1]; but to appreciate the circumstances under which these investigations were planned and executed, we must orient ourselves to the scientific environment at the turn of the century, particularly as it concerned the measurement of radiant energy and the theory of chemical structure.

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The Spectrometers

The fundamentals of spectroscopic optics were established before 1900, and most modern spectrometers are still based on these designs. In 1896 Wadsworth[2] published a series of articles on "The Modern Spectroscope" from which the present-day reader can acquire an excellent picture of instrumental theory and technique at the time with which we are concerned. The optical system used by Coblentz in the first, and smaller, of his two spectrometers is illustrated in Fig. 1. The prism and telescope remained fixed, and the spectrum was scanned by rotating the collimator-source unit. This instrument had a mirror of 35-cm focal length. In the earliest work on iodine[3] a hollow glass prism filled with carbon disulfide was used for measurements to 2.7 μ. Later, a rock-salt prism became available[4] and the measurements were extended to 15 μ.

For the work on organic compounds Coblentz also constructed a larger spectrometer using two mirrors of 1 meter focal length, and 20-cm aperture with the same rock-salt prism; this spectrometer gave twice the dispersion of the smaller one. Energy limitations prevented the use of this instrument beyond 7 μ, but many of the spectra were remeasured on this spectrometer over its useful wavelength range.[5] This instrument could be set up with the same optical arrangement as the smaller one, but alternatively it could be assembled in the Wadsworth mounting which provides for a fixed telescope and collimator and rotation of the prism; by this means all measurements are made at minimum deviation. Coblentz reported that both optical systems gave results in excellent agreement, but expressed no personal preference. Much time was occupied with matching the calibration of the smaller and larger instruments through their regions of overlap, and a troublesome systematic error was ultimately traced to the difference in the curvature of the slit image focused on the detector. We can sense Coblentz' feelings of relief when he could write:

> Applying this correction to about a dozen compounds, the location of the maxima, as found with

the small apparatus, coincided exactly with that found with the larger spectrometer.[6]

The Nernst heater, used as a radiation source, did not differ fundamentally from the heated oxide elements used today. Current was supplied from a storage battery of 90 cells. The heater element of the original Nernst lamp consisted of a hollow clay cylinder wound with platinum wire and covered with a thin coating of a second refractory material. Coblentz spent some time modifying the refractory layer, and reported the results in an Appendix to the Carnegie Monograph No. 32 ("Investigations of Infrared Spectra, Parts I and II"). Much later he returned to the study of the emission characteristics of the Nernst glower. This led to an extensive investigation of the emission spectra of metal oxides, and to close collaboration with the Nernst Lamp Company of Pittsburgh.[7]

His absorption cells for liquids would not seem out of place in a modern laboratory.[8] Windows were made by cleaving natural rock-salt plates and were used without polishing. Washers of tin foil or thin pieces of U-shaped wire were used as spacers. They were sealed with LePage's glue, and a spectrum of this was thoughtfully included in the monograph! The cell was mounted in a wooden holder that could be raised and lowered into and out of the beam. When raised, a compensating rock-salt plate replaced it in the beam. Since the whole source and sample unit moved radially with the collimator when scanning the spectrum, Coblentz could not conveniently employ a real image of the source to illuminate the entrance slit, and it is in this respect that his source optics differed from those of a modern instrument. The source itself was mounted on an extension of the collimator arm, only a few cm from the absorption cell. A shutter, constructed of sheet iron and asbestos, was located between the source and the

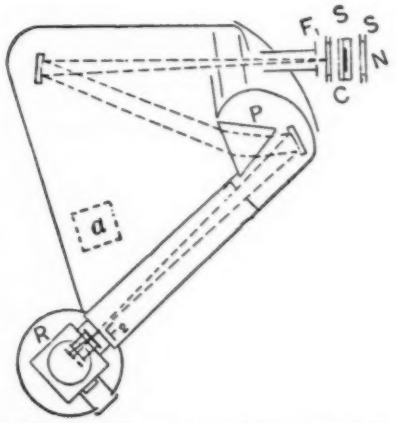

Fig. 1. Coblentz' smaller spectrometer as used in the work on iodine (ref. 4). F_1 is the movable arm with cell (C), shutters (S), and source (N); R is the radiometer. (By permission of the American Physical Society.)

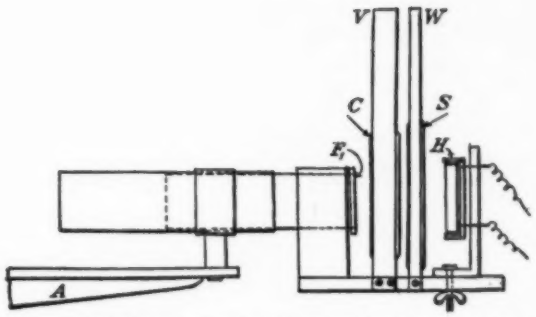

Fig. 2. Detail of the source and cell assembly as used in the work on organic compounds (ref. 5). H is the Nernst heater, S the sheet iron and asbestos shutter, and C the cell. The shutter and cells can be raised vertically by separate controls in the wooden guides W and V. (By permission of the Carnegie Institution of Washington.)

cell (Fig. 2). Both cell and shutter could be raised and lowered remotely by string and pulley mechanisms. Since Coblentz does not comment on any severe temperature effects on the sample, we must assume that the thermal insulation of the shutter was effective.

The radiometer detector was built by Coblentz with the advice of a fellow student, G. W. Stewart,[9] and was copied from the design of E. F. Nichols.[10,*] Essentially the "Nichols radiometer" consisted of a blackened mica vane supported by a quartz fiber in an evacuated space. The radiation impinged on the edge of the vane, and the rotatory displacement against the torque of the fiber was recorded by an optical lever. Experimental ability of high order was needed to construct a sensitive radiometer and, although Coblentz gives full credit to E. F. Nichols, he himself made significant modifications that helped to make this detector a practical working instrument. The earlier models suffered from troublesome effects due to the accumulation of static charges on the vanes. This occurred particularly with new instruments and at critical pressures during the evacuation. Coblentz associated this with the back diffusion of mercury vapor from the exhaust pump, and remedied it by inserting gold foil distributed over absorbent cotton into the vacuum line. He also increased the sensitivity by reducing the

* E. F. Nichols (1869–1924) should not be confused with E. L. Nichols (1854–1937) who, as Head of the Physics Department at Cornell University, supervised Coblentz' graduate work and initiated him into spectroscopy. E. F. Nichols had also been a student of E. L. Nichols at Cornell from 1888 to 1892, but the two men were not related. The radiometer was designed by E. F. Nichols in 1897 while working in Rubens' laboratory in Berlin. At the time Coblentz was constructing his radiometers E. F. Nichols was Professor of Physics at Dartmouth College, but there is nothing in Coblentz' published work that would indicate he had direct help from E. F. Nichols in their construction. In his autobiography Coblentz refers only to a single meeting with E. F. Nichols in 1907.[11]

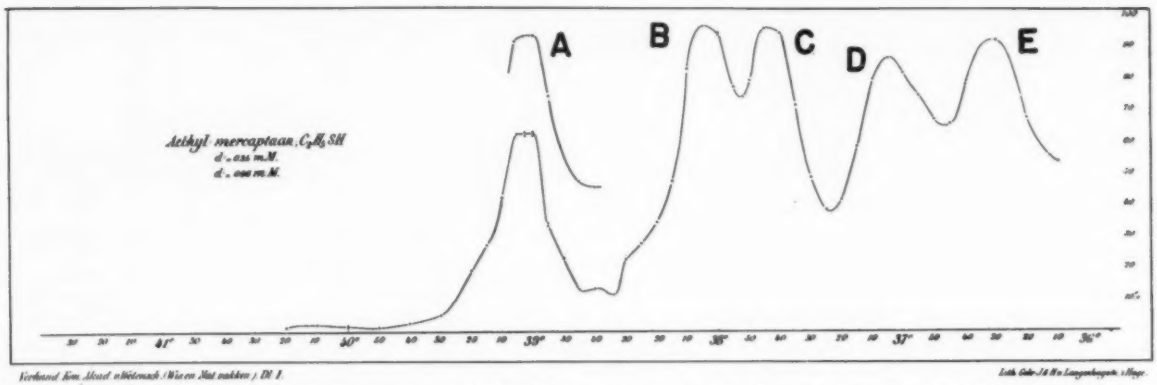

Fig. 3. Julius' spectrum of liquid ethyl mercaptan plotted as %-absorption upwards against the grating circle reading. (By permission of the Royal Netherlands Academy of Sciences and Letters.)

dimensions of the vane and was able to eliminate the outer window by improving the vacuum seals.

Wavelength Calibration

To the late nineteenth-century spectroscopists the mapping of the infrared spectrum in terms of the angular displacement of the prism or collimator was no longer a serious difficulty, but the conversion of the angle readings to wavelength measurements posed a problem. The ultimate calibration was necessarily based on the grating equation. The "anchoring" of the spectrum depended on the use of a foregrating to pass a series of overlapping orders into the spectrometer. Thus, in the classical experiment of Langley,[12] the D_2 sodium line at 0.5890 μ was excited in an electric arc, which provided a high background of infrared radiation. The sodium light was passed through a Rowland concave grating, and focused onto the entrance slit of a rock-salt prism spectrometer. Radiation of wavelengths corresponding to $n \times 0.5890$ μ entered the prism spectrometer and the prism angles corresponding to wavelengths for which $n = 1$ to 9 were established by observing maxima in the bolometer deflections. In this manner Langley mapped the infrared spectrum to 5.3 μ and computed the rock-salt dispersion curve. Later Paschen[13] determined the dispersion of fluorite to 9.43 μ and rock salt to 9.76 μ. In a paper in the same issue of the *Annalen der Physik und Chemie*, Rubens[14] published similar data and extrapolated the rock-salt indices to 12 μ.

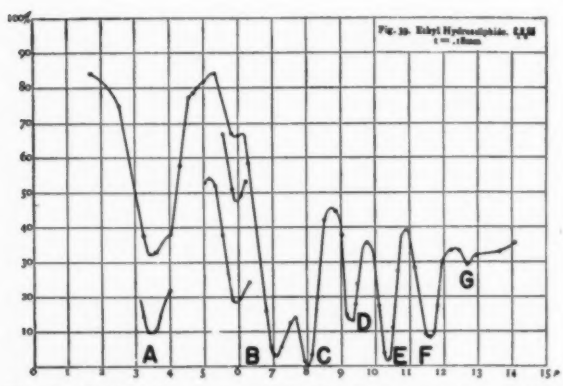

Fig. 4. Coblentz' spectrum of liquid ethyl mercaptan plotted as %-transmission upwards against the wavelength in microns. (By permission of the Carnegie Institution of Washington.)

Coblentz was fortunate in having these measurements available. The situation a short while earlier is well illustrated by the work of Julius,[15] who published the absorption spectra of twenty organic compounds in 1892. At that time only Langley's rock-salt dispersion curve to 5.3 μ had been reported, and Julius extrapolated this linearly. His spectrum for ethyl mercaptan is compared with Coblentz' curve and with a modern spectrum in Figs. 3–5. The good technical quality of Julius' spectrum is apparent, but the calculated band positions given in Table I are far out, while those of Coblentz agree well with the modern values.

In 1908 Paschen[16] revised his dispersion curve for rock salt and extended the measurements to 16 μ, which necessitated a change in some of Coblentz' radiant energy measurements. By this time, however, his interest in the organic compounds had waned, and Coblentz did not apply these small corrections to this earlier work. He was chagrined by this dependence on the Paschen data and annoyed by his inability, through circumstances beyond his control, to make dispersion measurements himself.[17]

Operating Technique

Having selected a setting of the spectrometer circle, Coblentz recorded the radiometer deflections using the cell-in cell-out technique; the ratio of the deflection gave the percentage transmission of the samples. Between each measurement the iron shutter was lowered and the radiometer zero checked. The time

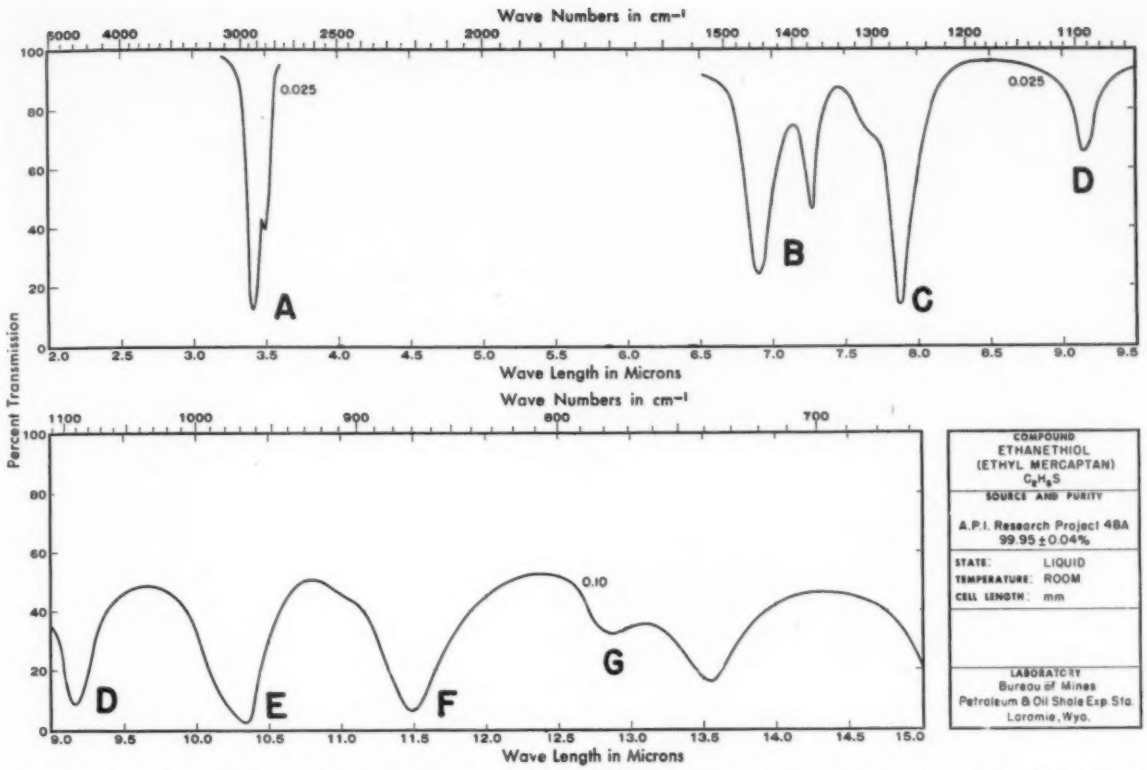

Fig. 5. Modern spectrum of liquid ethyl mercaptan plotted as Fig. 4. (By permission of the American Petroleum Institute.) (The original A.P.I. Chart No. 1112 has been edited to clarify the presentation.)

Table I. Positions of the Principal Absorption Bands in the Infrared Spectrum of Ethyl Mercaptan

	Julius[a]		Coblentz[b]	A.P.I. No. 1112[c]
		μ	μ	μ
A	39° 2.5′	(3.4)	3.45	3.40
B	38°. 5′	(8.5)	7.1	[6.89]
				[7.25]
C	37°. 45′	(10.2)	8.05	7.86
D	37°. 5′	(13.7)	9.25	9.15
E	36° 30′	(16.5)	10.34	10.30
F	—	—	11.6	11.48
G	—	—	12.65	12.86

[a] From ref. 15. Julius only tabulated his band positions in angular measurement though he did include an extrapolated rock-salt dispersion curve from which the wavelength positions might be estimated. Coblentz (ref. 5, p. 135) is perhaps overcritical of Julius in this respect.

[b] From ref. 5, p. 143.

[c] Spectrum supplied by the U.S. Bureau of Mines, Laramie, Wyoming.

Table II. Positions of Characteristic Band Maxima

	Coblentz' values[a]		Modern values[b]
	μ	cm⁻¹	cm⁻¹
CH_3 or $—CH_2—$	3.43	2910	2960–2850
	6.86	1460	1470–1460
	13.6–14	735–714	725–720
$—NH_2$	2.96	3380	3500–3310
	6.1–6.15	1640–1620	1640–1560
C_6H_6[c]	3.25	3080	3030
	6.75	1480	1500–1450
	8.68	1150	
	9.8	1020	1275–960[d]
	11.8	847	860–800[e]
	12.95	772	770–730[f]
$—NO_2$	7.47 ?	1340	1350–1250
	9.08	1100	?
—OH	2.95	3390	3600–3200
—NCS	4.78	2090	2175–2040

[a] From ref. 5, p. 117.

[b] From ref. 24.

[c] Coblentz drew no distinction between benzene and phenyl groups in various degrees of substitution.

[d] These bands are not very characteristic and the positions depend on the degree and position of substitution.

[e] Tetra-substituted with two adjacent hydrogen atoms.

[f] Mono-substituted.

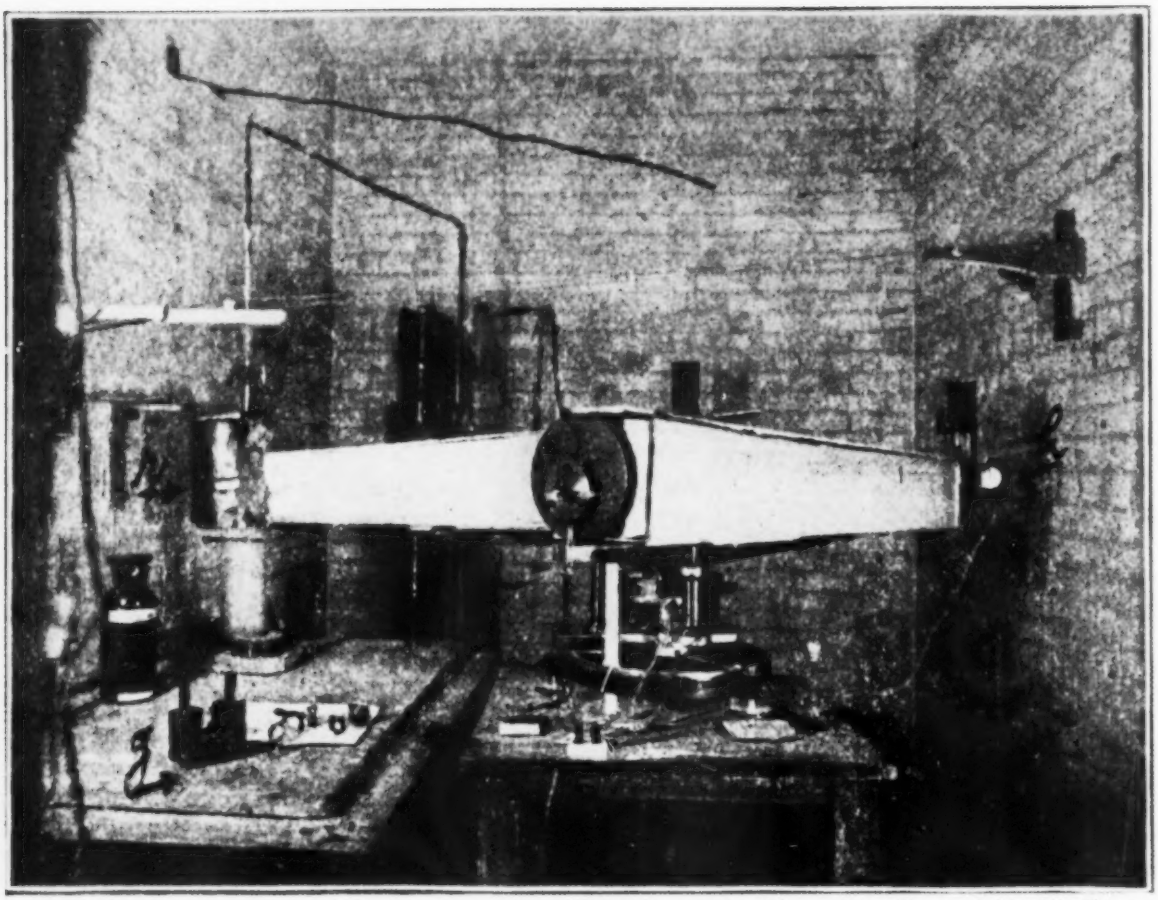

Fig. 6. Coblentz' larger spectrometer in the laboratory at Cornell University, reproduced from ref. 5. (By permission of the Carnegie Institution of Washington.)

required for a single transmission measurement was 1.5 minutes, and the exploration of the complete spectrum took from 3.5 to 4 hours. The operator sat in an outer room, manipulated the shutters and cells by means of the cables and plotted the spectrum at the same time. There does not appear to have been any provision for the remote resetting of the spectrometer circle between readings; this would seem to require his entering the inner room before each measurement, but apparently this did not significantly upset the thermal balance of the radiometer.

By this method of differential recording, compensation for atmospheric water vapor absorption was performed automatically. One might have expected that, with the long optical path and absence of atmospheric dehumidification, the energy in the 5 to 6 μ region would have been quite low. However, Coblentz makes no comment about this. In Table II of the Carnegie Institution Monograph No. 35 an illustrative set of experimental data is recorded. From this we can evaluate his I_0 values as a function of wavelength and these show no violent oscillations indicative of resolved water vapor structure.

In later life Coblentz looked with some disapprobation on the preoccupation of modern infrared spectroscopists with automatic gadgetry, and he has this to say on the subject[18]:

> Recently I was amused by the remark of a youth, who was just beginning to record infrared absorption spectra automatically, that he was surprised to find the wave lengths of the absorption maxima I published four decades ago 'so accurate'. Seeing that the automatic apparatus he was using had no spectrometer circle, and that its calibration was obtained by using the wave lengths of the maxima of absorption bands observed years ago, by orthodox methods, naturally there was good agreement with present observations! Until someone provides more reliable refractive indices (and their temperature coefficients) of rock salt and of fluorite, a correction of the 'Coblentz scale' (as one man called it; like the 'Rowland Scale') will remain in abeyance.

While this quotation is typical of Coblentz' dry humor, it also reveals that grating instrumentation did not hold much attraction for him, and even at this later date he appears to regard the grating primarily as a device for obtaining dispersion curves. It is regrettable that we do not have his comments on the recently published *Tables of Wavenumbers for the Calibration of Infra-red Spectrometers*[19] which are based exclusively on the direct measurement of spectra on grating spectrometers where the dispersion data for rock salt and fluorite play no part.

In Fig. 6 a photograph of Coblentz' laboratory at Cornell University is reproduced from the Carnegie Monograph No. 35 and in Fig. 7 is shown a collection of memorabilia from an early period at the United States Bureau of Standards, including three of the original bottles of organic chemicals brought with him from Cornell.*

Chemical Aspects of the Work

Coblentz' activities as an organic chemist were limited to the Cornell period. After his transfer to the Bureau of Standards in May 1905 his interests soon changed, and his subsequent work in infrared spectroscopy[20] dealt mainly with inorganic materials, particularly minerals. His limited formal training in organic chemistry shows up occasionally, as in his confusion between "hydrocarbons" and "carbohydrates".[21] Nevertheless, he clearly recognized that much of the work of the earlier spectroscopists was invalidated by the use of impure compounds, and he did all within his power to assure that the chemicals he employed were rigorously purified. His account of the procedures he used for the preparation of organic gases (ethane, ethylene, acetylene) would do credit to any organic chemist of the same era. His use of the infrared spectrum to follow the purification of ethane[22] is classical. As the preparation proceeds he notes the disappearance of bands at 8.25 and 10.5 μ. The former he attributes to the starting material, ethyl iodide; the latter could also be due to ethyl iodide or to ethylene.

Most of the late nineteenth century work on the infrared spectra of organic compounds was limited to measurement of overtone and combination bands in the 1 to 3-μ region, and it is therefore natural that these investigators should be impressed by the harmonic relations they observed among the wavelengths of the overtone bands. As measurements were extended into the region of the fundamental vibration frequencies the potential significance of these harmonic relations was reinforced by a numerical accident that locates the C—H stretching modes of methylene groups in alkane chains near 3.45 μ, the scissoring deformation mode near 6.83 μ, and the rocking mode near 13.9 μ, and thus places the most prominent absorption bands of many aliphatic organic compounds in a relation of 1:2:4. Coblentz became much preoccupied with this seemingly profound relationship.

Space does not allow a detailed analysis of his views on the band positions, but we can summarize his conclusions. His initial interest in these organic spectra was motivated by the desire to investigate the relation between the band positions and the molecular weight of the compounds. He rightly observed that the molecular weight *per se* played no great part in determining the pattern of absorption, which was much more influenced by the intramolecular structure. He noted, however, that *dextro-* and *laevo*-pinene gave identical spectra and thus showed that the absolute stereochemical configuration was not involved.

He observed also that the replacement of a hydrogen atom by $—NH_2$ or $—CH_3$ introduced characteristic changes in the spectrum and that a definite pattern was associated with the presence of a benzene ring. He concluded that the vibration of the benzene ring is not destroyed by incorporation into a more complex molecule, but he was hesitant to infer that the new bands resulting from the introduction of $—NH_2$, $—CH_3$ or the phenyl group were necessarily "due to the groups of chemical atoms substituted".[23] Although reluctant to commit himself to the concept of "group vibration frequencies" the idea was certainly present in his mind. He submitted a list of such "group frequencies" which are compared in Table II with the wavenumber ranges taken from a recent monograph.[24]

Coblentz' most telling illustration of the influence of localized molecular structure on the infrared spectrum

Fig. 7. Apparatus in Coblentz' laboratory at the Bureau of Standards, dating from the early infrared period at Washington (1905–1907). A mounted sodium chloride prism is shown on the left and a silver chloride prism on the right. In the center are three samples of the original chemical collection brought from Cornell University. A thermocouple and its evacuatable holder are in the foreground.

* I am grateful to E. K. Plyler for supplying this photograph.

was provided by his comparison among CH_3—S—C≡N, CH_3—S—N≡C, and C_6H_5—S—N≡C. In both the methyl compounds he notes bands at 3.4 and 7 μ and the appearance of a broad band near 4.8 μ common to all the compounds containing —N≡C and —C≡N. Of the phenyl compound he says, "This is the most important compound investigated, since it shows the superposition of the spectra of benzene and the mustard oils. We have not only the maxima of benzene at 3.25, 6.25, 6.75, 8.7, and 10 μ, but also the marked band at 4.8 μ which is common to all the mustard oils".[25] At this point Coblentz came close to opening up the whole field of organic structural analysis by infrared spectroscopy, and anticipating the developments which, in fact, started only twenty years later with the investigations of Lecomte.[26]

The present-day chemical spectroscopist would unhesitatingly designate the characteristic absorption of the carbonyl group in the 5.2 to 6.2 μ region as the most unequivocal and valuable "group frequency vibration". It is therefore curious that although many carbonyl compounds were included in the Coblentz collection, he failed to recognize the specificity of this absorption band and did not include it in his table. Many of these carbonyl bands show clearly in his spectra, e.g., methyl acetate, acetone, ethyl succinate, the straight chain fatty acids, phenyl acetate, benzaldehyde, cuminol, etc. The origin of this band in the carbonyl group is also demonstrated in his spectrum of acetyleugenol and by its absence from the eugenol spectrum. Coblentz notes this in the discussion of these two spectra[27] but draws no general conclusion.

Perhaps here, more than anywhere, Coblentz's limited appreciation of the problems of organic chemistry is in evidence. Though his observations on the specificity of the mustard oil spectra are significant spectroscopically, those compounds are to be classed as relatively unimportant chemical curiosities, or certainly were so to the chemists of that era. If he had placed more emphasis on infrared spectroscopy as a means of characterizing the oxygen containing functional groups he might have created more excitement in chemical circles, perhaps even enough to have persuaded him to continue working in this field. Coblentz was a physical Gilbert who failed to meet his chemical Sullivan. Such a partnership, building on these initial investigations, and guided by a chemically oriented mind, receptive to the problems of structural chemistry then ripe for solution, might have changed the whole course of modern organic chemistry. We must not, however, take Coblentz to task for what the chemist failed to do. The loss is theirs, not his.

Conclusions

While at this time we honor Coblentz for his magnificent technical achievement, we must be fair to the earlier investigators, and remember that Coblentz had the good fortune of building on the work of Rubens, Paschen, Langley, and E. F. Nichols, who had put the means to do this work at his disposal. Others, much earlier than he, had speculated on the possibility of determining molecular structure by vibrational analysis, but had lacked effective means to do so. It is therefore fitting that we conclude this article with a quotation from the much earlier paper of Abney and Festing, who, in 1881, measured the overtone absorption bands of organic compounds photographically.[28]

> We should have liked to have said more regarding the detection of the different radicals, but it might seem presumptuous on our part to lay down any general law on the results of the comparatively few compounds which we have examined. In our minds there lingers no doubt as to the easy detection of any radical which we have examined, but it will require more energy and ability than we possess to thoroughly classify all the different modifications which may arise. We may say, however, it seems highly probable by this delicate mode of analysis that the hypothetical position of any hydrogen which is replaced may be identified, a point which is of prime importance in organic chemistry.

Twenty years later Coblentz made these fancies facts, and now, with the passing of another sixty years these concepts and techniques have become part of the standard tools of trade of all organic chemists. Let us at least pay homage to our forebears.

The author is grateful to the publishers listed below for their kind permission to reproduce the diagrams and photographs as indicated: The American Physical Society (Fig. 1), The Carnegie Institution of Washington (Figs. 2, 4, 6), The Royal Netherlands Academy of Sciences and Letters (Fig. 3), and The American Petroleum Institute (Fig. 5).

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* The Carnegie Institution Monographs No. 35, 65, and 97 have been republished, in a single volume and are obtainable from The Secretary, The Coblentz Soc., c/o The Perkin-Elmer Corporation, Norwalk, Conn. (See page 1111 of this issue.)

Coblentz Memorial Prize

The Coblentz Society has decided to commemorate the memory of Dr. Coblentz' contribution to chemical infrared spectroscopy by awarding the Coblentz Memorial Prize—annually if financial considerations permit and a candidate of sufficient merit is available. The Prize will be awarded to younger workers in the field of chemical spectroscopy (no winner can be more than 36 years of age) to recognize and encourage their contributions in the field of chemical spectroscopy.

Applied Optics Reporters

These reporters submit information from which are compiled in part the news columns of *APPLIED OPTICS.* They have a rather thankless and seldom properly recognized task, and the *APPLIED OPTICS* editors are very grateful to them.

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Applied Optics January 1962

featuring **OPTICAL PUMPING AND MASERS**
editor B. H. Billings

Magnetic Resonance in Radiating or Absorbing Atoms—Francis Bitter
Composite Rod Optical Masers—G. E. Devlin, J. McKenna, A. D. May, and A. L. Schawlow
Atomes à l'Intérieur d'un Interféromètre Perot-Fabry—A. Kastler
Synthetic Maser Ruby—Robert D. Olt
Proposal for an Electron Accelerator Using an Optical Maser—Koichi Shimoda
Recent Developments in Maser Devices and Materials—Hendrik J. Gerritsen
The Interference between Beams from the Opposite Ends of a Ruby Optical Maser—P. Kisliuk and D. J. Walsh
Photomixing Experiments with a Ruby Optical Maser and a Traveling-Wave Microwave Phototube—B. J. McMurtry and A. E. Siegman
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Coblentz Memorial Lecture

The Coblentz Society's sponsored symposium will be replaced at the 15th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy (2-6 March 1964) by a Memorial Lecture by Sir Gordon Sutherland, FRS, director of the U.K. National Physical Laboratory. Short papers by invited speakers will complete the afternoon program.

The Influence of W. W. Coblentz on Radiometry

J. A. Sanderson

"There are few fields of experimental investigation so beset with difficulties as the quantitative measurement of radiant energy", wrote W. W. Coblentz in 1907[1] in one of his early papers on instruments and methods for radiometry. He then was 34 years of age and had been at the National Bureau of Standards a scant three years. Yet, since receiving his doctorate at Cornell University in 1903, he already had published some 33 papers and two books, mainly relating to the infrared region of the spectrum, and clearly he had set for himself the achievement of precision in radiometry as at least one of his variegated interests and concerns.[2]

His comment was far from being a complaint about tedium and the necessity for meticulous care with small detail. His papers were written in an age when brevity was not a fashion of scientific narrative, permitting attention to important minutiae. A review of them engenders the feeling, not at first but gradually as the reviewer progresses, that Coblentz had a feeling almost of affection toward all forms of radiation and all instruments which would register it. He was concerned with "fox-fire" and fireflies, with the sensitivity of the eye to various colors, and with the quantitative measurement (with distinguished associates) of erythemal ultraviolet radiation from the sun. But it is with methods of measurement in the infrared region of the spectrum that his name is most closely associated, and it is his work and his influence in this field to which we now owe much at a time when radiometry in one form or another and in one wavelength band or several is a prime means of geophysical and astronomical investigation from the surface of the earth, upwards through the atmosphere, and into space.

It is not intended to convey the impression that Coblentz alone established the instruments and the methods for quantitative radiometry; indeed, merely to read the references in one of his many papers is to recall the names of great men who laid the strong foundation of thought and experimentation which undergirds our current endeavors. Coblentz did not originate new devices of measurement; rather, he built and used and evaluated and attempted improvements upon the radiomicrometer, the Nichols radiometer, the metal strip bolometer, and the radiation thermopile, the latter of which emerged from his work as an instrument of standard measurement and basic calibration not yet displaced and unlikely to be.

It is of interest that, in the emerging science of absolute, quantitative measurement of radiation, early workers were less concerned with minimum detectable radiant power in watts than with the minimum change in temperature of the detector that could be detected. This was of the order of 10^{-6} to 10^{-5} °C. The early writings of Coblentz (and of others) specified sensitivity in this term, often without auxiliary data to permit convenient estimation of the radiant power incident on the detector. Response was expressed in terms of deflection in centimeters of a galvanometer or radiometer at a scale distance of one meter when the source was a standard sperm candle one meter from the detector, or when it was a Hefner Lamp.

It is a little difficult to learn from the literature, without more study than has been given to it in the preparation of this paper, precisely when this practice gave way to the more fundamental notion that it is the quanity of detectable incident radiant power, and not its effect on the detector, that is of concern. It surely commenced with the early determination of the Stefan-Boltzmann constant by Kurlbaum in 1898 or before. By 1914 Coblentz[3] had begun to assess various standards of radiation critically in terms of irradiance, or flux density of radiation, in W/cm² at stated distances from the detector, measured by comparison with a blackbody radiator, and to suggest the use of seasoned carbon incandescent lamps as secondary standards of radiation with the plea that:

> . . . . .it is desirable to emphasize the importance of specifying the intensity of a radiation stimulus in accurate units so that an experimenter's work can be repeated. . . . In this manner a better agreement will be attained between theory and experiment, and radiometry may attain a dignity comparable with other lines of investigations.

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Received 6 May 1963.

He established the reliability of these secondary standards in an impressive way by recording that two of them were intercompared after a lapse of seven months with an experimental deviation of only 0.3% from former measurements, and with this deviation attributable in part to the circumstance that the later measurements were made on a "windy day". Twelve additional lamps were subsequently found to agree with their original calibrations, after six months, within one to three parts in 1000! Thus, criteria for radiometric precision have long been available; they hinge on meticulous attention to every detail of the complex radiation environment from source to detector.

By 1916, Coblentz and Emerson[4,5] had published their first paper on the determination of the Stefan-Boltzmann constant, σ, utilizing a bismuth-silver thermopile placed quite near a blackened manganin strip, which was the receiver of radiation from a blackbody furnace. The manganin strip, warmed by radiation from the furnace, radiated in turn to the thermopile. Then the furnace was shut off by a water-cooled shutter between two water-cooled diaphragms through which the thermopile viewed its radiant scene. Coblentz properly made much in his papers of these water-cooled diaphragms and shutters by way of emphasizing the importance of measuring *only* the source when all of nature is radiating in the same spectral region. The source being thus shut off, the manganin strip was heated electrically to produce the same thermocouple response; in this manner σ was determined in terms of established standards of voltage and current.

A summary of his work on σ, and on c_2, the second radiation constant, is to be found in the *Journal of the Optical Society of America*.[6] One may today examine as many handbooks as he has available and find just that many different values of σ and of c_2. This is, of course, not the fault of physics, but the nature of it as a science of ever improving approximations. Coblentz well recognized this and wrote somewhere of the risk of considering any experimental value as final. In the matters of measuring the total radiation constant and the second radiation constant it would seem difficult to improve on his work. It has had durable influence on our knowledge of the most probable values of the various fundamental constants,[7] and it provides a

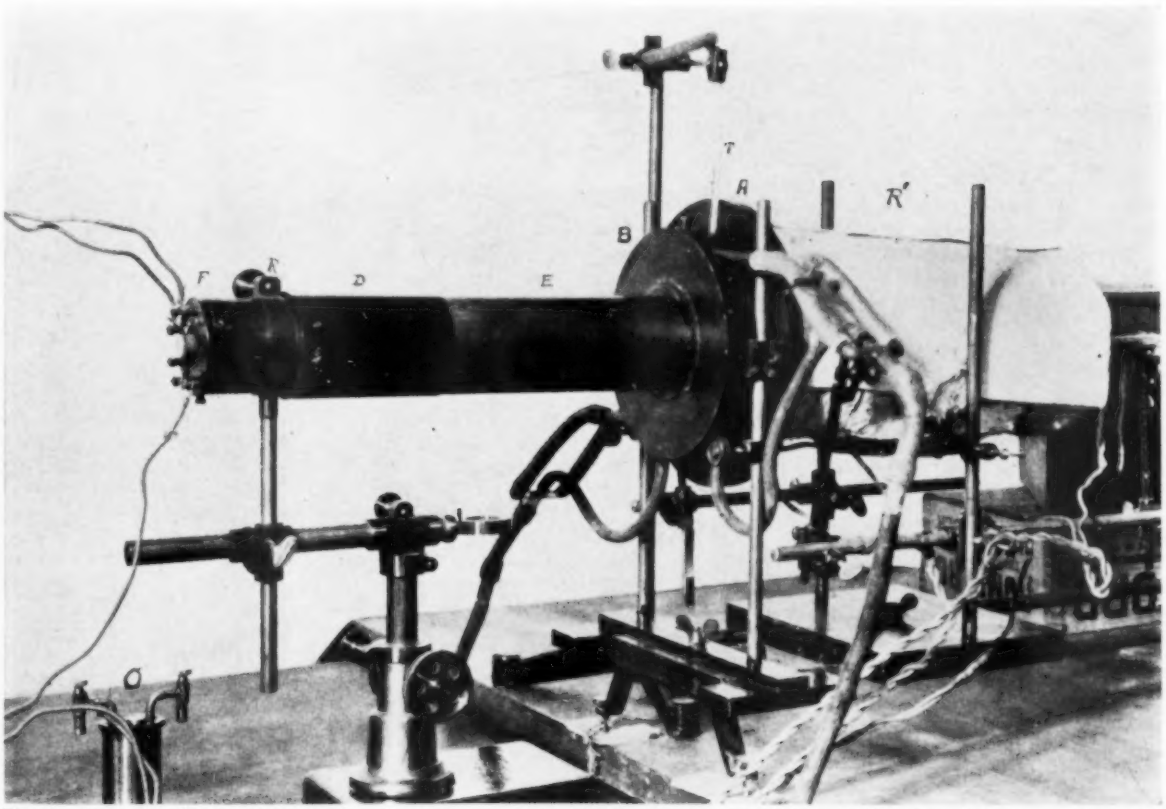

Fig. 1. Apparatus for the determination of σ. R was an electric furnace run at 1000° ± 0.1°C. A and B were water-cooled diaphragms between which was a water-cooled shutter. The modified Angstrom pyrheliometer was at F. Telescoping tubes D and E permitted adjustment of distance. Galvanometer deflections were repeatable to a few tenths of a millimeter.

lasting example of the sheer pleasure that is to be enjoyed in the accomplishment of precise physical measurement.

In an era when the outward appearance of scientific instruments offered for sale seems often to preoccupy both purveyor and purchaser as much as the contents of the package, a picture of the Coblentz "outfit"—as he called it—with which he made his precision measurements of the total radiation constant may be of interest. It is shown in Fig. 1.

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3. W. W. Coblentz, Bull. Bur. Standards **11,** 87 (1914).
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7. R. T. Birge, Revs. Mod. Phys. **1,** 1 (1929).

Applied Optics — Of Optics and Opticists

This column is compiled partly from information sent by our Reporters in various centers of optics across the continent, but the Managing Editor welcomes news from any source

> I can trace my ancestry back to a proto-plasmal primordial atomic globule. Consequently my family pride is something inconceivable. *W. S. Gilbert*

University research and patent policy. During the past two years, the Office of Patent Policy has been making a comprehensive survey and interpretative analysis of the current policies, practices, and procedures of universities, colleges, institutes of technology, and independent professional schools in the United States with respect to the conduct of scientific and technological research and the handling of discoveries and inventions resulting from such research. This project has been supported by grants from the NIH and a contract from ONR. The results of the survey have been published by the NAS—NRC under the title "University Research and Patent Policies, Practices, and Procedures" (NAS—NRC Publication **999,** 291 pp., 1962). Designed to provide factual information for the guidance of university and college administrators, research scientists, government officials, foundation executives, industrialists, patent management agents, and others concerned with the administration, conduct, and support of nonprofit scientific and technological research and with the disposition of patentable discoveries and inventions growing out of such research, the publication covers the current practices of 945 institutions of higher education and discusses 147 formalized research and patent policies in effect as of July 1962.

A Yale University astronomer has solved a problem which has concerned astronomers for a century. Since the 1850's, astronomers have been trying to understand why there are (Kirkwood) gaps in the band of asteroids that lie between Mars and Jupiter, in addition to those predicted for Saturn's rings. **Dirk Brouwer's** explanation for the Kirkwood gaps in the asteroid belt predicts that Saturn's rings should show a number of faint, dark divisions, in addition to the large ones already visible to a telescope, caused by the planet's inner moons, Miman and Enceladus. Dr. Brouwer reports his work in the April 1963 issue of the Astronomical Journal [**68,** 152 (1963)].

The **University of Rochester's** College of Engineering is now the College of Engineering *and Applied Science,* to "reflect more accurately the increasingly science-oriented programs of the College", also to take into account certain quasi-legal implications because three departments of the College—chemical, electrical, and mechanical engineering—are licensed as professional engineering units by the New York State Education Department, while the fourth department—optics (which became a department of the engineering school in 1961)—is officially designated as an applied science.

Science Fair, New Mexico s .w OSA give two prizes this year—first to Roger Rensvold for laser action in fluid media, and second to Robert Waber for "design and operation of an experimental spectrograph"; honorable mentions went to Thomas Norris, Terry Beard, and Philip Paden. . . .The Office of Aerospace Research offered summer employment to six of the Science Fair participants who were selected to receive USAF recognition at the 14th Science Fair—International last May in Albuquerque. They had the opportunity to work as laboratory aides to AF scientists engaged in basic research.

Other **OAR** news this month is that high-speed color motion pictures of the human vocal cords have been taken for the first time at a frame rate of over 9000 pictures per second by AFCRL scientists **Henry I. Soron, Sheldon B. Michaels, and Philip Lieberman.** The c..or movies clearly show the onset and end of the brief transition vocal sounds that normally occur in speech. . . .AFCRL people are developing a compact, lightweight instrument which will give direct readings of the refractive indices of the atmosphere at microwave frequencies (1000 to 3000 Mc/sec). Presently, refractive indices are determined by computation of simultaneous readings from instruments measuring pressure, temperature, and moisture. The AFCRL development will, it is hoped, result in an instrument light enough to be lifted by conventional weather-sounding balloons. . . .An infrared interferometer developed by AFCRL and carried aboard an AF satellite gave AFCRL scientists the sharpest view yet obtained of the continuously varying temperature patterns of the earth and chemical constituents of the atmosphere. The infrared interferometer satellite experiment was carried out under the direction of **Louis Block.** . . .On 15 April there was a major reorganization of the **Air Force Cambridge Research Laboratories.**

continued on page 1131

On the Astrophysical Work of W. W. Coblentz

John Strong

Coblentz says in his autobiography[1] that astronomy had such a special fascination for him as an undergraduate at Case, that the study of it became an obsession. Subsequently, as a student at Cornell, he was assigned the responsibility of reporting articles in the *Astrophysical Journal*, in a graduate seminar. This assignment helped prepare him for applications of radiometry to telescopic observations later, after he had acquired a leading competence in radiometry.

His early work in infrared spectroscopy, and the culmination of it in determining Planck's constant c_2 (thus confirming the radiation laws), provided him with the specialty that gave significance to his pioneering, and later work, in astrophysics.

He elaborated this eagle's territory of infrared radiometry to include ultraviolet photometry, which he applied to studies of the solar ultraviolet spectrum. Much of this ultraviolet research related to stratospheric ozone, and we shall not touch on it further, for his work with the thermocouple in astrophysics overshadowed it.

Two circumstances bear significantly on his first move into astrophysics: Professor Pfund, at Johns Hopkins University, anticipated him in measuring a star's heat with a thermocouple. Pfund did this in 1913, using the Naval Observatory refractor. Also, Coblentz' efforts to obtain the use of the 60-in. (152-cm) Mt. Wilson telescope were unsuccessful because of competing astronomical projects.

The first circumstance only stimulated him. Indeed, the results he got during his eighteen nights of observations with the Crossley Reflector at Lick Observatory in 1914, were the first scientifically significant results. There he measured 110 stars together with planets and nebulae, and showed that red stars emitted two to three times as much total radiation as blue stars of the same magnitude (as expected from the radiation laws).

It is interesting, parenthetically, that the Crossley Reflector was involved in Coblentz' 1914 thermocouple work. This pioneer, reduction-to-practice, large reflecting telescope has been involved in many firsts. For example, it was the first large reflector to be aluminized.

At the beginning Coblentz, in his interest in planetary temperatures, was largely alone (now, who is not interested?). Coblentz resumed his telescopic research at Lowell Observatory in 1921, seven years after the Lick work. At Lowell, with Lampland, he found the high temperatures of the dark hemisphere of Venus. The 100-in. (254 cm) telescope at Mt. Wilson, giving sixfold greater light-gathering power than the 100-cm telescope available at Lowell, gave Coblentz stimulating competition. Mt. Wilson also became active in stellar and planetary radiometry; and there Nicholson and Pettit anticipated Coblentz in the thermal study of the dark hemisphere of Venus.

However, at Lowell, Coblentz started the series of observations of the heat radiation emitted by the planet Mars which were so extensive that recently they have served as a basis for making "weather maps" for Mars. The area of the thermocouple receiver he used to probe the temperatures of Mars was two orders of magnitude smaller than the area of the planet's disk that was focused on it.

A filter method of separating spectral components had been suggested by H. N. Russell and was used for the observations at Lowell and Mt. Wilson before the 200-in. (508 cm) studies in 1954, when a spectrometer was used. In the beginning D. H. Menzel collaborated with Coblentz in interpretation of the Lowell observations.

The studies of Martian temperatures thus begun by Coblentz in 1922 were continued, paced by the timing of oppositions, by Coblentz and Lampland in 1925–1926; and by Lampland on through 1943. Pettit and Nicholson studied the temperatures of Mars (1924, 1925, 1930) with the 254-cm telescope at Mt. Wilson; and Strong and Sinton covered the 1954 opposition bolometrically, using the 508-cm telescope at Mt. Palomar.

One of the prime results of the observations of Coblentz *et al.*, aside from their intrinsic interest, is that the temperatures adduced from the observations have

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served as a kind of dew-point hygrometer (correlating Martian temperatures with the morning disappearance of frost) to determine the amount of water vapor in the Martian atmosphere.

About one-tenth of Coblentz' papers were devoted to astrophysical radiometry. He was a pioneer in development of portable thermocouples for this use; and in refinements of the galvanometer to display thermocouple response. He lived to see radiometric study of the planets become popular.

Reference

1. W. W. Coblentz, *From the Life of a Researcher* (Philosophical Library, New York, 1951).

Meetings Calendar

November

7–9 Acoustical Soc. of Am., Ann Arbor *G. Peterson, U. of Mich., Ann Arbor, Mich.*

12–14 AFIPS, Fall Joint Computer Conf., Los Angeles, Calif. *P. Huggins, AFIPS, P.O. Box 55, Malibu, Calif.*

12–15 Magnetism and Magnetic Materials Conf., Atlantic City, N.J. *J. D. Blades, Burroughs Corp. Res. Center, Paoli, Pa.*

13–15 5th Ann. Eastern Analytical Symp., Statler Hilton Hotel, NYC *R. F. O'Connell, Sperry Rand Research Center, Sudbury, Mass.*

20 OSA Chicago Sect., Photoplastic Recording by S. Aftergut *C. R. Lambrecht, 7729 N. Ashland Ave., Chicago, 31, Ill.*

December

4 OSA Natl. Capital Sect. Mtg., Georgetown U., Indian Dyes by W. R. Brode *H. K. Hammond III, NBS, Wash. 25, D.C.*

9–12 1963 Fall URSI Mtg., U. of Wash., Seattle *M. G. Morgen, Dartmouth Col., Hanover, N.H.*

26–31 AAAS, 130th Ann Mtg., Cleveland, Ohio *AAAS, 1515 Mass. Ave. N.W., Wash. 5, D.C.*

1964

— Colloquium on Magnetism, Nottingham, England *IUPAP, Institut d'Optique, 3 boul. Pasteur, Paris 15e, France*

January

19–24 ACS Natl. Mtg., Denver, Colo. *ACS, 1155 16th St. N.W., Wash. 6, D.C.*

22–25 12th Ann. Physics Show, Statler-Hilton Hotel, N.Y.C. *T. Vorburger, AIP, 335 E. 45 St., N.Y., 17, N.Y.,* APS *K. K. Darrow, 538 W. 120 St., N.Y. 27, N.Y.,* and APPT *E. U. Condon, Oberlin Col., Oberlin, Ohio,*

29–31 Am. Meteorological Soc., Ann. Mtg., Los Angeles *AMS, 45 Beacon St., Boston 8, Mass.*

February

19 OSA Natl. Capital Sect. Mtg., Johns Hopkins Homewood Campus, Baltimore, Spectroscopic Research at JHU by G. H. Dieke *H. K. Hammond III, NBS, Wash. 25, D.C.*

19 OSA Chicago Sect. Mtg., Axicons and Their Uses by J. H. McLeod *C. R. Lambrecht, 7729 N. Ashland Ave., Chicago 31, Ill.*

March

2–6 15th Pittsburgh Conf. on Analytical Chem. and Appl. Spectroscopy, Pittsburgh, Pa. *J. O. Frohliger, Duquesne U., Pittsburgh 19, Pa.*

4–6 Thermal Radiation of Solids Symp., Sheraton-Palace Hotel, San Francisco *W. D. Harris, Eng. & Sci. Ext., U. of Calif., Berkeley 4, Calif.*

15–21 Am. Soc. of Photogrammetry, Am. Cong. on Surveying and Mapping, Washington, D.C.

April

— OSA Natl. Capital Sect. Mtg., Georgetown U., Far Infrared Optics by R. C. Lord *H. K. Hammond III, NBS, Wash. 25, D.C.*

— Internatl. Measurements and Instruments Conf., 3rd, Stockholm *G. Ljungberg, Royal Swedish Acad. of Engin. Science, Box 5073, Stockholm, Sweden*

— Am. Ceramic Soc. Glass Div. Chicago *J. Rood, Bausch & Lomb, Rochester 2, N.Y.*

1–3 **Optical Society of America Spring Meeting, Sheraton-Park Hotel, Washington, D.C.** *M. E. Warga, OSA, 1155 16th St. N.W., Wash. 6, D.C.*

5–10 ACS Natl. Mtg., Phila., Pa. *ACS, 1155 16th St. N.W., Wash. 6, D.C.*

5–10 Asia-Pacific Acad. of Ophthalmology, 2nd Cong., Melbourne *R. N. Mellor, 82 Collins St., Melbourne, C1, Australia*

12–17 SMPTE, 95th Semiann. Conv., Los Angeles, Calif. *SMPTE, 55 W. 42 St., New York 36, N.Y.*

28–May 2 SPSE Internl. Conf. of Photographic Science and Engineering, American Hotel, N.Y.C.

May

— Soc. of Technical Writers and Publishers, 11th Ann. Conv., San Diego, Calif.

4–5 Inter-Soc. Color Council, Statler-Hilton Hotel, NYC *R. M. Evans, Eastman Kodak Co., Rochester 4, N.Y.*

5–9 15th Natl. Science Fair-Internatl., Baltimore, Md. *Science Service, 1719 N St. N.W., Wash. 6, D.C.*

2nd week French Soc. of Ophthalmology, 71st Cong., Paris *M.-A. Dollfus, Soc. Française d'Ophthalmologie, 27, rue du Faubourg-St.-Jacques, Paris 16, France*

19–21 APS, Norman, Okla. *W. A. Nierenberg, U. of Calif., Berkeley 4, Calif.*

19–21 Internatl. Symp. on Microwave Theory and Techniques, L.I., N.Y. *S. Rosenthal, PIB Grad. Center, Farmingdale, N.Y.*

20–23 Acoustical Soc. of Am. NYC *W. Waterfall, 335 E. 45 St., New York 17, N.Y.*

25–29 French Soc. of Physical Chem., 14th Ann. Mtg., Bordeaux *G. Emschwiller, Soc. de Chimie Physique, 10, rue Vauquelin, Paris 5, France*

26–28 CIBA Found. Symp. on Physiology & Experimental Psychology of Color Vision, London *41 Portland Pl., London W. 1, England*

26–28 AFIPS, Spring Joint Computer Conf., Washington, D.C. *P. Huggins, AFIPS, P.O. Box 55, Malibu, Calif.*

June

— APS, summer mtg., Denver, Colo. *K. K. Darrow 538 W. 120 St., New York 27, N.Y.*

7–13 European Opthalmological Soc., 2nd Cong., Vienna *J. François, 15 place de Smet de Naeyer, Ghent, Belgium*

8–10 PIB Symp. on Quasi-Optics, Statler-Hilton Hotel, N.Y.C. *L. Felsen, Polytechnic Inst. of B'klyn, 55 Johnson St., B'klyn 1, N.Y.*

15–26 AFOSR Seminar on Communications and Cybernetics, Cloudcroft *J. R. Foote, P.O. Box 1053, Holloman AFB, N.M.*

A Redetermination of Some Optical Properties of Calcium Fluoride

Irving H. Malitson

This paper gives refractive-index values at 24°C for a synthetic and a natural prism of calcium fluoride. Measurements were made by the minimum-deviation method at 46 calibrated wavelengths from 0.23 μ in the ultraviolet to 9.7 μ in the infrared. The indices of the synthetic prism were fitted to a three-term Sellmeier dispersion formula of the form: $n^2 - 1 = \Sigma A_j\lambda^2/(\lambda^2 - \lambda_j^2)$. Dispersive quantities were computed which estimate the expected relative dispersion, chromatic aberration, and resolution of CaF_2 as a function of wavelength. Values of dn/dt are also given. The results of this work are compared with previously reported data.

I. Introduction

Calcium fluoride has for many years been an important material used in the design of optical components and systems. Many of the early workers, notably Paschen, Martens, Carvallo, Langley, Rubens, Micheli, and Liebreich, who investigated the optical properties of fluorite during the latter part of the 19th century and early years of this century, made refractive-index measurements on a number of specimens of the natural crystal, presumedly by different methods and at various temperatures. Most of these data have been referenced and compared and can be found in the literature.[1] Coblentz reduced the measured and computed values of Langley, Paschen, and Rubens to a common temperature of 20°C and after careful analysis adopted a table of index values from a smooth curve drawn through these data. This table of refractive index is thought to represent the most accurate and comprehensive values available in the literature.[2]

Synthetic calcium fluoride has been available commercially for approximately fifteen years and is being produced by an increasing number of crystal growers; nevertheless, comprehensive index values outside the visible region of the spectrum have not been published for the synthetic crystal. It is the purpose of this paper to present the results of index measurements made for both the synthetic and natural crystal over a wide range of wavelengths, on a single instrument, by use of identical procedures for different wavelength regions, and to compare these data with those of the early workers.

Three prisms of synthetic fluorite and one of natural fluorite were used in these investigations. The synthetic material was developed by Stockbarger[3,4] in the early 1940's. He considered the synthetic fluorite to be "comparable with good natural fluorite in all essential properties". The natural fluorite prism has been at the National Bureau of Standards for more than fifty years and is believed to be of European origin.

II. Index Data

In 1944, refractive indices were determined at the National Bureau of Standards for two samples of the synthetic crystal for nine visible wavelengths at temperatures of 15°, 35°, and 55°C. These measurements were made on a Geneva Society spectrometer equipped with a housing for precise control of the temperature. The averaged index values of both prisms, published previously by Stockbarger[3,4] are reproduced in Table I. The uncertainty of these index measurements is estimated at 2×10^{-6}.

The third synthetic prism, fabricated from a Stockbarger grown crystal deposited at NBS, was investigated in 1959. This prism has face dimensions approximately 55 × 73 mm and a refracting angle near 70°. The prism was measured on a precision minimum-deviation spectrometer modified for measuring refractive index at visible and nonvisible wavelengths. This instrument, shown schematically in Fig. 1, is equipped with a reflecting optical system, a device for

The author is with the National Bureau of Standards, Washington, D.C.

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Table I. Index of Refraction of Synthetic CaF_2 and Thermal Coefficient of Index per °C

(Average of two prisms in 1944)

Wavelength (μ)	Index of refraction			$-dn/dt \times 10^6$	
	15°C	35°C	55°C	15–35°C	35–55°C
0.767858[a]	1.430984	1.430768	1.430546	10.80	11.10
0.7065188	1.431763	1.431553	1.431331	10.50	11.10
0.6678149	1.432356	1.432142	1.431922	10.70	10.85
0.6562793	1.432545	1.432335	1.432114	10.50	11.05
0.589262[a]	1.433893	1.433683	1.433465	10.50	10.90
0.5460740	1.435023	1.434813	1.434593	10.50	11.00
0.4861327	1.437106	1.436894	1.436680	10.60	10.70
0.4358342	1.439555	1.439354	1.439143	10.05	10.55
0.4046563	1.441573	1.441378	1.441168	9.75	10.12
Abbe No.	95.13	95.13	94.93		

[a] Intensity weighted mean of doublet.

scanning the spectrum at a uniform rate, a Golay pneumatic detector, a signal amplifier, and a recording potentiometer.

The refractive-index measurements were made at controlled room temperatures near 14°C and 24°C over a wavelength range from 0.2288 μ in the ultraviolet to 9.724 μ in the infrared. The calibrated wavelengths for which indices were determined are those of various emission sources and absorption bands. These are listed in columns 1 and 2 of Table II. The experimentally determined index values at 24°C were plotted as a function of wavelength and are shown in Fig. 2. These values were also fitted to a three-term Sellmeier dispersion equation of the form $n^2 - 1 = \Sigma A_j\lambda^2/(\lambda^2 - \lambda_j^2)$, where n is the refractive index, the λ_j's represent

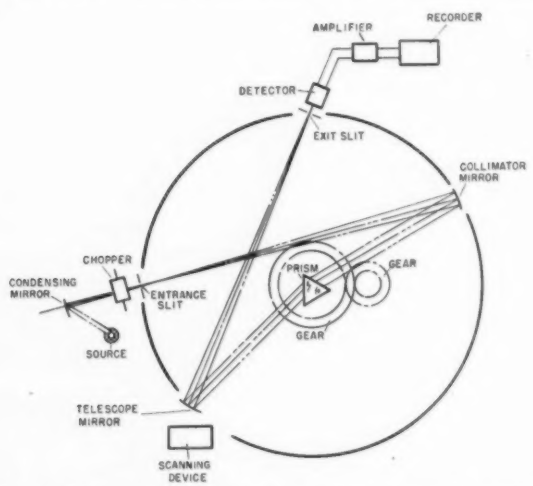

Fig. 1. Schematic diagram of the modified Gaertner precision spectrometer showing optical path. The prism is rotated at one-half the rotation rate of the telescope assembly by gear system, thus maintaining the condition of minimum deviation for any wavelength. The scanning device drives the assembly which scans the spectrum to identify lines or bands and determines their approximate scale positions.

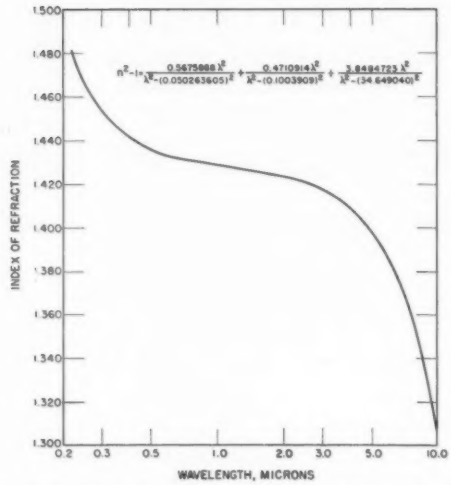

Fig. 2. Refractive index of synthetic CaF_2 at 24°C as a function of wavelength. The dispersion formula is valid for interpolation over the measured wavelength range.

ultraviolet and infrared absorption wavelengths located beyond the range of the measured wavelengths and the A's are related to the strengths of the absorption bands. The parameters of the equation, shown in Fig. 2 and listed in Table III, are determined very accurately by a least-squares solution performed by a programmed electronic computer. A detailed account of the method may be found in the literature.[5,6] The accuracy of fit of this equation is shown in Table II where the indices computed by the equation (column 3) and the differences between the observed values (column 4) are listed. The average of the absolute values of the residuals for 46 measured wavelengths is 2.46×10^{-5} with only three residuals larger than 5×10^{-5}. At wavelength $\lambda = 0.2537$ μ, where the residual is $+9 \times 10^{-5}$, there is observational uncertainty because emission lines of cadmium, zinc, and mercury are present in the spectral source. In the 6-μ region of the infrared, where the larger residuals occur, exact wavelength identification was confusing because in this region there are many overlaying atmospheric water-vapor bands present.

The dispersion formula was used to compute values of refractive index n at 24°C at wavelengths separated by regular, small intervals. The equation was then differentiated with respect to λ, and the resulting algebraic expression for the slope of the curve, $dn/d\lambda$, which is a negative quantity, was computed at the same wavelengths. These data are listed in Table IV.

The natural fluorite sample investigated in this experiment is of good optical quality and has faces about 50 × 50 mm and a refracting angle near 60°. This prism was measured at 24°C over the same spectral range. The data were compared with the observed and computed index values for the synthetic crystal

Table II. Computed Index of Refraction of CaF_2 and Residuals $(o\text{-}c) \times 10^5$ at 24°C; Also Thermal Coefficient of Index for Mean Temperature of 19°C

λ (μ)	Source	Computed index	Synthetic $o\text{-}c$	Natural $o\text{-}c$	$-dn/dt \times 10^6$
0.228803	Cd	1.47635	−2	+1	6.2
0.24827	Hg	1.46793	+3	+5	7.0
0.2537	Hg	1.46602	+9	+12	7.5
0.26520	Hg	1.46233	−1	0	8.1
0.28035	Hg	1.45828	−1	+1	8.4
0.296728	Hg	1.45467	−2	0	8.8
0.334148	Hg	1.44852	−1	+2	9.2
0.34662	Cd	1.44694	−3	0	9.4
0.365015	Hg	1.44490	−4	0	9.6
0.4046563	Hg	1.44151	−3	+1	9.8
0.4358342	Hg	1.43949	−3	0	10.0
0.4861327	H	1.43703	−4	0	10.2
0.546074	Hg	1.43494	−3	+1	10.4
0.589262	Na	1.43381	−2	+2	10.4
0.643847	Cd	1.43268	−2	+3	10.4
0.6562793	H	1.43246	−2	+1	10.4
0.6678149	He	1.43226	−1	+1	10.5
0.7065188	He	1.43167	−2	+2	10.5
0.767858	K	1.43088	−2	+2	10.6
0.85212	Cs	1.43002	−1	+4	10.6
0.8944	Cs	1.42966	0	+1	10.6
1.01398	Hg	1.42879	−2	0	10.5
1.3622	Hg	1.42691	+1	+8	10.0
1.39506	Hg	1.42675	+1	+6	9.9
1.52952	Hg	1.42612	+4	+4	9.6
1.7012	Hg	1.42531	+2	+4	9.4
1.81307	Hg	1.42478	0	+9	9.1
1.97009	Hg	1.42401	+3	+3	8.9
2.1526	TCB[a]	1.42306	−1	+1	8.7
2.32542	Hg	1.42212	+3	+4	8.5
2.4374	TCB	1.42147	0	+2	8.5
3.3026	Poly[b]	1.41561	0	+3	8.2
3.422	Poly	1.41467	+2	+2	8.1
3.5070	Poly	1.41398	−1	+2	8.0
3.7067	TCB	1.41229	+2	+2	7.8
4.258	CO_2	1.40713	+4	+4	7.5
5.01882	H_2O	1.39873	+1	+5	7.3
5.3034	TCB	1.39520	+3	+3	7.2
6.0140	H_2O	1.38539	+5	+5	7.0
6.238	Poly	1.38200	−6	0	7.0
6.63306	H_2O	1.37565	0	+1	6.9
6.8559	H_2O	1.37186	−8	+2	6.7
7.268	MCH[c]	1.36443	+2	+7	6.5
7.4644	H_2O	1.36070	+5	+6	6.4
8.662	Poly	1.33500	−4	+3	6.0
9.724	Poly	1.30756	+1	+5	5.6

[a] TCB = 1,2,4-Trichlorobenzene.
[b] Poly = Polystyrene.
[c] MCH = Methylcyclohexane.

Table III. Constants of the Dispersion Equation at 24°C

$$n^2 - 1 = \Sigma A_j\lambda^2/(\lambda^2 - \lambda_j^2)$$

$\lambda_1 = 0.050263605$	$\lambda_1^2 = 0.002526430$	$A_1 = 0.5675888$
$\lambda_2 = 0.1003909$	$\lambda_2^2 = 0.01007833$	$A_2 = 0.4710914$
$\lambda_3 = 34.649040$	$\lambda_3^2 = 1200.5560$	$A_3 = 3.8484723$

Table IV. Computed Refractive Index and Dispersion of CaF_2 at 24°C for Regular Wavelength Intervals

λ(μ)	n	$-dn/d\lambda$	λ(μ)	n	$-dn/d\lambda$
0.22	1.48110	0.5819	1.60	1.42579	0.0046
0.24	1.47120	0.4206	1.80	1.42484	0.0048
0.26	1.46391	0.3155	2.00	1.42385	0.0050
0.28	1.45836	0.2437	2.20	1.42280	0.0054
0.30	1.45402	0.1926	2.40	1.42168	0.0057
0.32	1.45056	0.1553	2.60	1.42049	0.0061
0.34	1.44775	0.1272	2.80	1.41921	0.0066
0.36	1.44548	0.1056	3.00	1.41785	0.0070
0.38	1.44349	0.0888	3.20	1.41639	0.0075
0.40	1.44185	0.0755	3.40	1.41484	0.0079
0.42	1.44045	0.0648	3.60	1.41320	0.0084
0.44	1.43924	0.0560	3.80	1.41147	0.0089
0.46	1.43820	0.0489	4.00	1.40963	0.0094
0.48	1.43728	0.0429	4.20	1.40770	0.0099
0.50	1.43647	0.0379	4.40	1.40567	0.0104
0.52	1.43575	0.0337	4.60	1.40354	0.0109
0.54	1.43512	0.0302	4.80	1.40130	0.0114
0.56	1.43454	0.0271	5.00	1.39895	0.0119
0.58	1.43403	0.0245	5.20	1.39650	0.0125
0.60	1.43356	0.0222	5.40	1.39394	0.0130
0.62	1.43313	0.0203	5.60	1.39127	0.0136
0.64	1.43275	0.0185	5.80	1.38849	0.0141
0.66	1.43239	0.0170	6.00	1.38559	0.0147
0.68	1.43206	0.0157	6.20	1.38258	0.0153
0.70	1.43176	0.0145	6.40	1.37945	0.0159
0.72	1.43148	0.0135	6.60	1.37620	0.0165
0.74	1.43121	0.0126	6.80	1.37282	0.0171
0.76	1.43097	0.0118	7.00	1.36932	0.0178
0.78	1.43074	0.0111	7.20	1.36569	0.0184
0.80	1.43052	0.0104	7.40	1.36193	0.0191
0.82	1.43032	0.0098	7.60	1.35804	0.0198
0.84	1.43013	0.0093	7.80	1.35401	0.0205
0.86	1.42995	0.0088	8.00	1.34983	0.0212
0.88	1.42977	0.0084	8.20	1.34552	0.0219
0.90	1.42961	0.0080	8.40	1.34106	0.0226
0.92	1.42945	0.0077	8.60	1.33645	0.0234
0.94	1.42930	0.0074	8.80	1.33169	0.0242
0.96	1.42915	0.0071	9.00	1.32677	0.0250
0.98	1.42901	0.0068	9.20	1.32168	0.0258
1.00	1.42888	0.0066	9.40	1.31643	0.0266
1.20	1.42771	0.0052	9.60	1.31101	0.0275
1.40	1.42672	0.0047	9.80	1.30541	0.0284

and found to be higher in each case by an average value of 2.83×10^{-5}. The differences between the observed values for the natural crystal and the computed values for the synthetic crystal are shown in Table II.

III. Dispersive Characteristics

The availability of high-speed electronic computers also makes practicable the calculation of three dispersive quantities from the values of n and $dn/d\lambda$ of Table IV. These measures of dispersion, shown graphically in Fig. 3, provide an indication of the expected dispersive characteristics of fluorite at different parts of the spectrum.

The quantity $(dn/d\lambda)/(1 - n)$ is analogous to $(nF - nC)/({}^nD - 1)$, the "dispersive power" of a prism as

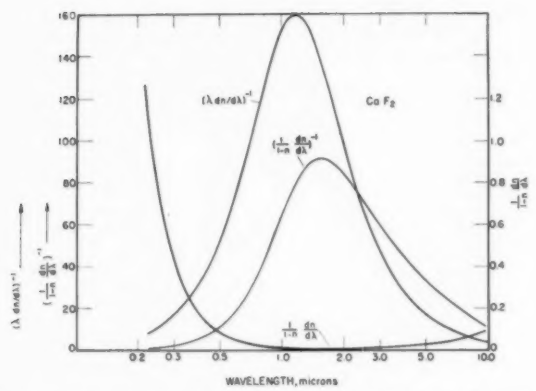

Fig. 3. Dispersive characteristics of synthetic CaF_2 as a function of wavelength. Relative dispersion reaches a minimum near 1.5 μ. Chromatic aberration decreases as value of $[(dn/d\lambda)/(1-n)]^{-1}$ increases. Expected resolution improves as value of $(\lambda dn/d\lambda)^{-1}$ decreases.

defined for the visible region of the spectrum. It is a measure of dispersion relative to deviation. The graph of this quantity shows that the relative dispersion decreases steadily with increasing wavelength, reaches a minimum in the neighborhood of 1.5 μ, then slowly increases again as it approaches the long wavelength cutoff. The quantity $[(dn/d\lambda)/(1-n)]^{-1}$, the reciprocal relative dispersion, corresponds to the Abbe number of a substance which is a datum used in correcting for chromatic aberration. An increase in this parameter represents a reduction of chromatic aberration in a lens material. Considering the whole range of wavelengths, the curve suggests that for the purpose of lens design chromatism can be minimized in the region near 1.5 μ. Boutry[7] has shown that for prismatic materials the relative "resolving power" at any wavelength λ is directly proportional to $\lambda dn/d\lambda$. It follows that for a given prism the larger the value of this quantity the better the expected resolution at λ. However, it is more convenient to use the reciprocal $(\lambda dn/d\lambda)^{-1}$; therefore, the best performance may be expected in the wavelength regions where the magnitude of $(\lambda dn/d\lambda)^{-1}$ is as small as possible. It can be seen that for the wavelength range under consideration the expected regions for useful resolution are at wavelengths shorter than about 0.5 μ in the visible and longer than about 3.0 μ in the infrared. Comparison of prism materials for use in the infrared[8] has shown that CaF_2 is an excellent choice in the wavelength range from about 4.0 to 9.0 μ.

Although there are other materials which are suitable for prisms in this infrared region, they are efficient over narrower wavelength intervals. The choice of CaF_2 as a compromise material avoids the need of a multiplicity of prisms and prism interchanges when used in spectroscopic apparatus.

These dispersive quantities suggest that for a specific material there are optimum regions of the spectrum for dispersion, low-chromatic aberration, and resolution. They provide, therefore, suitable information for estimating the expected optical performance of a material.

IV. Thermal Coefficient of Index

The observed averaged indices and observed temperatures listed in Table I were used to calculate the thermal coefficient of index for the range 15°C to 35°C and for the range 35°C to 55°C. These values, also listed in Table I, show that in the visible region increases in temperature result in decreased indices of refraction. It can also be seen that the absolute value of dn/dt tends to increase with increasing wavelength and temperature. Thermal coefficients of index were also de-

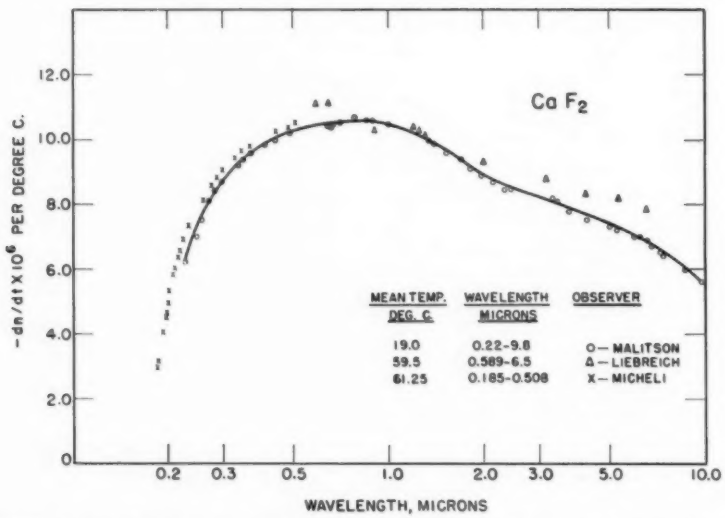

Fig. 4. Comparison of NBS thermal coefficients of index with those of other observers. An average value of $-dn/dt$ for the temperature interval of 15°C to 24°C over the entire measured wavelength range is 8.65×10^{-6}.

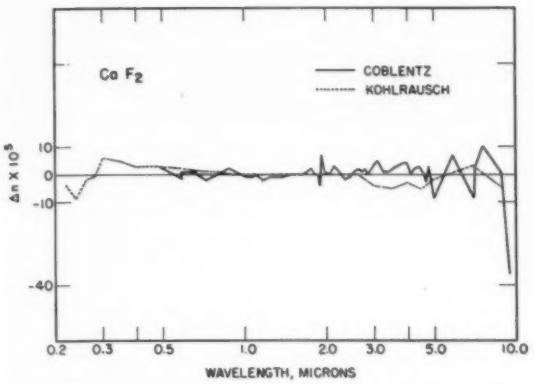

Fig. 5. Comparison of computed NBS index values at 20°C of synthetic CaF_2 with previously reported values for the natural crystal. The NBS values are represented by the line $\Delta n = 0$.

termined for the synthetic prism from the recent index measurements made at 14°C and 24°C. These values of dn/dt for the mean temperature of 19°C are given in Table II (column 6) and are plotted as the solid curve in Fig. 4. The curve has a steeper slope in the ultraviolet than in the visible region which indicates that the ultraviolet absorption bands are probably shifted nearer the visible as the temperature is increased. The thermal coefficients, as in the visible region, are negative over the entire measured spectral range. However, the values of dn/dt tend to become less negative as the wavelengths get shorter which suggests that the values of dn/dt for calcium fluoride, like those for sodium chloride, might assume a positive value near the extreme of the transmitting range. The decrease of dn/dt in the infrared indicates that the infrared absorption bands also have shifted toward longer wavelengths with increasing temperature. The dn/dt values of Micheli[9] for a mean temperature of 61.25°C for wavelengths from 0.185 to 0.508 μ and those of Liebreich[10] for a mean average temperature of 60° from 0.589 to 6.5 μ are plotted for comparison purposes. This comparison confirms the observations made by these observers that for fluorite and certain other crystals the absolute value of dn/dt increases with increasing temperature.

V. Discussion

The Sellmeier formula used in this experiment is considered to be primarily a mathematical fit of the measured data. The residuals obtained by the formula indicate that values of index may be interpolated to five decimal places. In order to compare the NBS values for the synthetic material with the data compiled by Coblentz for the natural crystal, it was first necessary to compute by formula of Table III values of index at a number of wavelengths intermediate to the discrete wavelengths listed in Table II. The resulting values were then adjusted to 20°C, the temperature of the literature values, using the thermal coefficients of index listed in Table II. Similarly, the formula's values were compared with another table of index data for natural material compiled by Kohlrausch.[11] These values were computed at regular wavelength intervals from a dispersion equation deduced by Paschen and also refer to a temperature of 20°C. Figure 5 shows the results of this comparison, the computed NBS values being represented by the line $\Delta n = 0$. The average difference between the NBS values and those of Coblentz and Kohlrausch is 2.18×10^{-5} for 57 wavelengths and 2.36×10^{-5} for 28 wavelengths, respectively. Part of this difference may be due to experimental error. The good agreement between NBS and Kohlrausch data at the longest wavelength indicates that Coblentz's value at that point may be in error.

VI. Conclusion

In this report, the determinations of refractive index and dn/dt for synthetic CaF_2 are only for these particular melts developed by Stockbarger. As far as can be judged from this investigation, the lack of uniformity of refractive index of both the synthetic and natural fluorite is of the order of 3×10^{-5}. This excellent agreement between samples demonstrates that the artificial crystal, when properly synthesized, should be comparable in refractive properties to good natural fluorite.

In closing, it is fitting to remember the late W. W. Coblentz who was an outstanding pioneer in the investigation of spectral radiation. This experiment has demonstrated that the table of values for CaF_2, adopted by Coblentz over forty years ago, has provided optical workers with reliable refractive index data.

The author thanks Patricia Page for her excellent translations of several German papers pertinent to this investigation and Fred V. Murphy for technical assistance. Special thanks to Loyd E. Sutton for evaluating the constants of the dispersion equation.

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Color in Business, Science, and Industry. By DEANE B. JUDD AND GUNTER WYSZECKI. Wiley, New York, 1963, 2nd ed. 500 pp. $15.00.

This revision of Judd's decade-old book bearing the same title presents much new material which is both informative and stimulating. The addition of Dr. Wyszecki as Dr. Judd's collaborator reinforces the previously won position of this volume as the most authoritative and comprehensive treatise on many parts of the science of color measurement.

In outline, and at a casual glance, this edition appears much like the earlier one. In both editions the first part deals with the eye and with the basic concepts of color space, color matching, and color perception. Part II, innocently titled "Tools and Technics", contains far more than a description of the physical and mathematical apparatus for color measurement and specification: in this part the reader will also find many of the fundamental contributions which have been made by both authors to the understanding of color space. The third part describes some of the effects of surface structure and of thickness, concluding with a valuable review of the dependence of reflectance on absorption and scattering coefficients and of their relation to colorant formulations. On closer examination the reader will find that a very large part of the earlier edition has been rewritten; some important new sections have been added, and a number of parts have been shortened or omitted. In Part I, the main addition is a brief review of theories of color vision. In Part II, there seems to have been a conscious attempt to eliminate those details which would become obsolete as technology develops, and to include instead more discussions of the underlying principles. For instance, where the earlier edition provided considerable details regarding the design of the most commonly used color-measuring instruments, the new one eliminates most of these details and gives in their place a discussion of some of the design factors to consider in selecting a measuring instrument. While the reasons for the change in approach can be appreciated, the loss in detail may well be regretted by many readers.

This difference in approach is perhaps more sharply illustrated by a comparison of the treatment of the very important subject of color differences in the two editions. In a few instances use is made of numerical color difference data to illustrate subjects under discussion, and the units used are in these cases always NBS units. Both editions present the formulas for computation not only of NBS units, but also of a number of other color-difference units which have been used or proposed. In a summarizing discussion of the several formulas in the new edition, the authors state that, of the various formulas, "the Adams Chromatic value equation should be used . . . if the data are in the form of tristimulus values X, Y, Z, such as result from reduction of spectrophotometric data by means of the 1931 CIE standard observer". It has in fact become a widespread practice in industry to employ this Adams equation, to multiply by a factor which is commonly between 40 and 50, and to call the result "NBS units". This procedure is so common as to deserve a comment from Dr. Judd as originator of the NBS unit. There is, however, in the new edition, no information on the relation between the size of the Adams unit and the NBS unit. It therefore becomes impossible to utilize the recommended equation in a manner which permits relating it to the NBS unit, without also referring either to the first edition or to some other suitable text.

Following the discussions of color-difference formulas, there is a new and valuable discussion of the metric of uniform color space. It is however to be regretted, in this reviewer's opinion, that even though this concept of the metric of uniform color space is today widely applied in industry as a basis of color-difference specification, and even though the authors' discussion of uniform color-space clearly implies some merits of this approach, there is not in the text any explicit indication of the procedure by which the concept of the metric of uniform color space can conveniently be used as a basis of color-difference description. Thus the reader will find that not only in the details regarding the selection and convenient use of the optimum mathematical methods, but also in the selection of optimum instrumentation, the new edition generally provides less detail on the working tools, but strives rather to give him the best background to make his own decisions. This procedure may be pedagogically meritorious, but it significantly reduces the value of the volume to the many users in business and industry who are urgently in need of recommended practices. This limitation becomes particularly important because the new edition, even more than the earlier one, very commonly assumes a greater mathematical and especially a greater geometrical sophistication than can be expected of its readers.

The new edition is greatly strengthened by several new sections, including particularly the discussions of the colorimetry of fluorescent materials, the effect of ten-degree observing fields, the introduction of the concept of degree of metamerism, the effects of chromatic adaptation, and the evaluation of color-rendering of light sources.

The assessment of degree of metamerism which is introduced in this volume represents an important subject which will urgently require further development in the coming years. Surely the general recognition in the past two decades of the significance of metamerism has contributed greatly to the ability of industry to make increasingly effective use of colorimetry, and the general acceptance of the term "metamerism" has been important in facilitating this recognition of its importance. Since the act of assigning a suitable name to a concept contributes to the development of that concept, this reviewer cannot refrain from commenting on the introduction by Judd and Wyszecki of a new term which appears to have some most unfortunate consequences. They introduce and frequently apply the words "isomeric pair", "isomeric differences", and "isomerism". An "isomeric pair", for instance, is a pair of lights (or colors) which, having identical spectral properties, are always an exact match. (Another term for "isomeric pair" might therefore be "identical pair".) The other terms are defined by inference, and surprising inferences can be drawn from their material. Thus, if the first introduction (p. 107) of "isomeric difference" constitutes an implied definition of the term, it is immediately evident that it would be possible that two colors, both of which present isomeric differences relative to a third color, may not represent an isomeric difference with respect to one another, a condition which appears to this reviewer to be quite unacceptable. During a subsequent discussion (pp. 155–156), it appears that an "isomeric difference" might also be called a "nonmetameric difference". According to the dictionaries (e.g., the *Shorter Oxford English Dictionary*, second edition), metamerism is defined as "(chem.) the condition of those *isomeric* compounds which, although of the same composition and molecular weight, have different chemical properties". Similarly, the *Merriam-Webster* (unabridged first edition) defines *isomeric* as being in one usage the same as metameric. Although it is true that this is a differently intended application of the words, surely there are enough words available so that it is not necessary for "isomeric" to mean "metameric" to a chemist, and yet to mean "nonmetameric" to a physicist. For these reasons it appears to this reviewer that the term "isomeric" cannot be usefully employed in colorimetry.

continued on page 1139

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The Use of Infrared Spectra of Chars in Coal Structure Research

R. A. Friedel

Indirect studies in the structure of coal and related carbonaceous materials are made through spectral studies of chars of model compounds. Temperature effects are demonstrated; the higher the temperature, or the longer the pyrolysis time, the higher the rank of coal that the char spectrum resembles. Charring of model compounds with and without oxygen present permits the assignment of some infrared bands of chars to oxygenated structures. Chars prepared from isotope-labeled compounds also permit the assignment of spectral bands through observation of isotopic shifts.

Infrared spectroscopy has been used for several years to study the structure of complex carbonaceous materials such as coals and various types of carbons. Indirect studies of coallike structures can be made through infrared spectral investigations of chars of model compounds. A char is defined as the benzene-insoluble residue from pyrolysis of any substance. The first paper on this subject appeared in the 1953 special number of the *Journal of the Optical Society of America* issued in honor of W. W. Coblentz.[1] It is fitting to report further work on char studies in this commemorative issue. Although the pioneering investigations of Coblentz did not encompass coal, he did study related substances such as "asphaltum", lampblacks, graphite, diamond, and carborundum.[2]

The 1953 article[1] demonstrated the close similarity between the spectra of bituminous coal and of carbohydrate chars. Carbohydrates remain among the best model compounds of the many examined for producing coallike chars.[1,3–6] The principal absorption bands encountered in the spectra of coals and chars (Fig. 1) usually include the OH and CH stretching bands around 3000 wavenumbers (cm^{-1}), aliphatic CH bending at 1450 and 1370, broad phenolic absorption at 1250, aromatic bands at 860, 810, and 750, and the most intense band at 1610 cm^{-1}, which is variously assigned to chelated carbonyl structures and/or aromatic rings.

It is commonly thought that a char from almost any material will give a coallike infrared spectrum, but this is not the case. Chars prepared from various carbohydrates and similar oxygen-containing compounds at 300–500°C invariably produce spectra having the strongest band near 1610 cm^{-1}. Not all of these chars will show the other characteristic coal bands, particularly the aromatic bands at 860, 810, and 750 cm^{-1}. Carbohydrate chars all show these bands. Early work indicated that a sizable percentage of hydroxyl groups in the starting material is necessary to produce a coallike char. Chars made from compounds with few or no aliphatic hydroxyl groups did not show the typical aromatic bands. Recently, however, linoleic acid, a C_{18} unsaturated acid with no hydroxyls other than that in the carboxyl group, has been found to produce a coallike char at 400°C.

Effect of Temperature

The correspondence of the spectra of coal and carbohydrate chars exists over a range of temperatures and of ranks of coal; for example, the aromatic bands in the spectra of cellulose charred at 300, 400, and 500°C resemble, respectively, the aromatic bands in the spectra of lignite (70 % C), bituminous (85 % C), and anthracite (92 % C) coals (Fig. 1). Thus, increasing temperature appears to produce an increase in "coalification". Another temperature effect can be seen in Fig. 1 in the aliphatic carbonyl region at 1730 cm^{-1}. Charring at 300°C and below produces a strong carbonyl band at 1730 cm^{-1}. A weaker band is observed at 1610 cm^{-1}. At 400°C and more definitely at 500°C the 1730 cm^{-1} band becomes weaker, and the 1610 cm^{-1} band becomes more intense. This appears to be due to a conversion from a simple to a complex carbonyl structure.

Spectral Effects of H and O in Chars

The study of char spectra has been broadened beyond the collection and correlation of model substances that will produce coallike chars. The spectral effects of specific elements, hydrogen and oxygen, in

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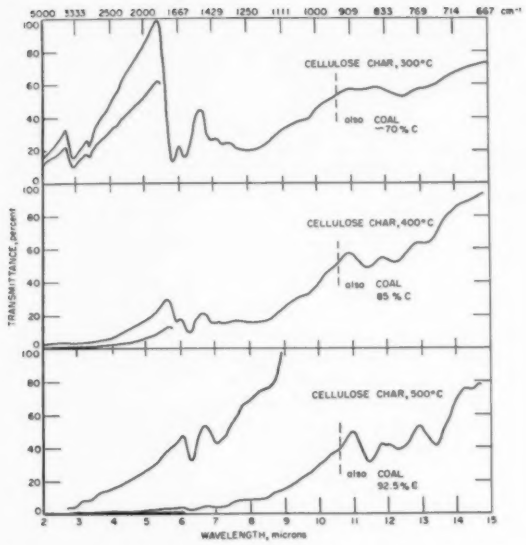
5000 3333 2500 2000 1667 1429 1250 1111 1000 909 833 769 714 667 cm⁻¹
CELLULOSE CHAR, 300°C
also COAL —70% C
CELLULOSE CHAR, 400°C
also COAL 85% C
CELLULOSE CHAR, 500°C
also COAL 92.5% C
TRANSMITTANCE, percent
WAVELENGTH, microns

Fig. 1. Infrared spectra of cellulose chars at various temperatures; portions of spectra to the right of the dashed line at 940 cm^{-1} are nearly identical to the spectra of specific coals, as indicated. Per cent transmittance values refer to the partial spectra above 1667 cm^{-1}; other spectra are expanded in order to enlarge the absorption bands.

chars are being studied. For investigation of the role played by a particular element, two approaches have been utilized: (1) studies of chars prepared from the same compound, with and without one element present (e.g., compounds charred with and without oxygen present); and (2) studies of chars prepared from compounds labeled with deuterium.

Attempts were made to determine the role of oxygen in the spectra of chars by pyrolyzing hydrocarbons in vacuo and also in oxygen. The spectrum of a char prepared from an aromatic hydrocarbon, anthracene, in vacuo at 500°C had no absorption bands that are typical of coal (Fig. 2). A char prepared from a C_{28} aliphatic hydrocarbon, *n*-octacosane, at 450°C in vacuo, does produce most of the typical coallike spectrum (Fig. 3); however, the spectrum is not completely coallike as the most intense coal band, 1610 cm^{-1}, is one of the weakest bands in the char spectrum. This finding indicates that a major part of the intense 1610 cm^{-1} band might be due to a nonhydrocarbon structure; the weak 1610 cm^{-1} band that does occur in the octacosane char may be due to aromatic structures.

Oxygen was introduced into these chars by forming them in the presence of air. Pyrolytic oxidation of anthracene and *n*-octacosane produces spectra with strong coallike 1610 cm^{-1} bands (Figs. 2 and 3). These data appear to confirm that the 1610 cm^{-1} band in these chars is mainly attributable to a chelated carbonyl structure. The similarity of the spectra of the oxygen-containing chars from anthracene and *n*-octacosane indicates that most of the absorption bands are due to oxygenated structures.

One set of experiments has been carried out on a substance labeled with a stable isotope. In an attempt to assign certain infrared absorption bands, particularly the aromatic bands, a completely deuterated paraffin was charred in the presence of oxygen (Fig. 4). The aromatic bands did not appear in the usual 730–910 cm^{-1} spectrum of the char; they were shifted by approximately the factor $(m_H/m_D)^{1/2}$ to the region of 530–650 cm^{-1}.[7] Other chars show no absorption in this region; coals show absorption here, but it is assignable to minerals rather than to organic structures. Thus, the so-called aromatic bands in the spectrum of coal are apparently assignable to vibrations involving hydrogen atoms, most probably on aromatic rings.

Broad absorption occurs at the 1450 cm^{-1} CH bending region, even though the deuterated char is essentially free of CH groups. This finding is another good indication that the 1450 cm^{-1} band in the coal spectrum is not due entirely to C—H vibrations.[8] It is probably due chiefly to ring vibrations of polysubstituted aromatics. A band at 1610 cm^{-1} is strong in the deuterated char and is assigned to a chelated carbonyl structure.

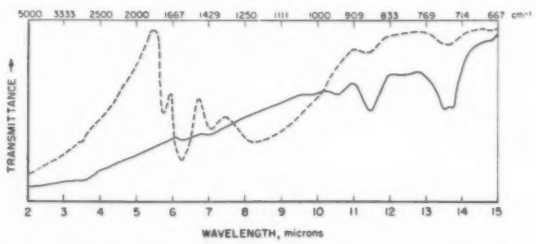

Fig. 2. Infrared spectra: —— anthracene char, 500°C in inert atmosphere; - - - anthracene char, 500°C in air after preheat at 300°C in air.

Additional labeling experiments are planned. In particular, labeling will be applied to the question of the 1610 cm^{-1} band. The fact that the spectrum of the char from linoleic acid is nearly identical to the coal spectrum will be utilized by charring linoleic acid, O^{18}. If the 1610 cm^{-1} band is due to a chelated carbonyl structure, a measurable shift of about 35 cm^{-1} to lower frequency will be observed for the labeled char.

Slow Pyrolysis at Low Temperature

Other char experiments for the investigation of rates of reaction are being carried out. Two substances, cotton and pine sawdust, have been heated in air at 200°C for 10 months. Treatment at this temperature for a few hours causes little change in these substances other than slight oxidation. However, after 10

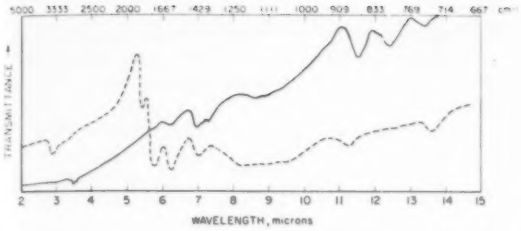

Fig. 3. Infrared spectra: —— *n*-octacosane char, 450°C in inert atmosphere; - - - *n*-octacosane char, 450°C in air after preheat at 350°C.

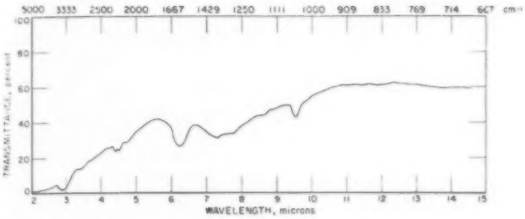

Fig. 4. Infrared spectrum of char from a deuterated paraffin, 450°C.

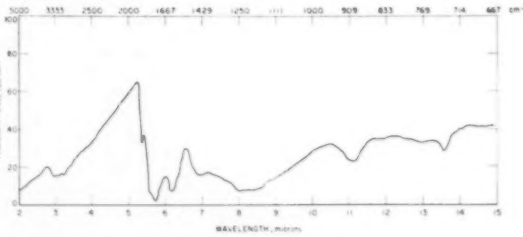

Fig. 5. Infrared spectrum of char from cellulose heated at 200°C in air for 10 months.

months the spectrum in Fig. 5 shows that char formation has occurred, and no similarity to the starting material remains. Even the 1610 cm^{-1} coal band is intense. The importance of time in coalification is thus indicated by these experiments; as Montgomery has pointed out in studies of the origin of crude oils, high-temperature reactions can occur at low temperatures when the time involved is extremely long.[9]

Similar slow pyrolyses of *n*-octacosane in air at 150°C have also demonstrated the gradual development of a 1610 cm^{-1} band. After 5 months a weak band was observed; at 15 months it was moderately intense and still growing. The 1730 cm^{-1} carbonyl band was intense at 5 months and became weaker with time as the 1610 cm^{-1} band became stronger. Thus, time and temperature produce the same spectral effect in the carbonyl region.

The assistance of physicist J. A. Queiser and chemist R. Raymond is gratefully acknowledged.

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The Publications of W. W. Coblentz on Infrared Spectroscopy

The principal work of the late W. W. Coblentz on infrared spectroscopy originally appeared in three Publications of the Carnegie Institution of Washington. Publication No. 35, issued in 1905, dealt with his investigations at Cornell University of the infrared absorption spectra of some 135 organic compounds, with shorter supplementary sections on transmission and reflection spectra. Publication No. 65 (1906) and Publication No. 97 (1908) are concerned with later work on the transmission and reflection spectra of minerals and other inorganic compounds carried out at the U.S. Bureau of Standards.

These classical investigations form the basis of most modern work on analytical infrared spectroscopy. The journals have long been out of print, but, with the kind permission of the Carnegie Institution, they have recently been reprinted in a single volume under the joint sponsorship of the Coblentz Society and the Perkin-Elmer Corporation.

All concerned with modern applications of infrared spectroscopy to problems of chemical structure and analysis should be conversant with this early work, which provides the basis for much of the modern technique. To maintain a properly balanced outlook on the subject, this volume should accompany the standard modern texts on the library shelf of the spectroscopy laboratory.

A limited number of copies of the first reprinting are still available at $3.50 per copy on application to Dr. H. B. Kessler, The Secretary, c/o The Perkin-Elmer Corporation, Norwalk, Connecticut.

Papers to appear in subsequent issues

Infrared Transmission through Fogged Salt Windows—*Morrow and Turk*

A Simple Grating Calibrator for the Visible and Vacuum Ultraviolet—*Hammer, Arakawa, and Birkhoff*

The Use of Polarized Infrared Radiation in Magneto-optical Studies of Semiconductors—*Palik*

An Optical Null Double-Beam Double-Pass IR Spectrophotometer—*Minami*

A Photomultiplier Circuit for Precision Spectrophotometry—*Budde*

Large-Scale Photoelectric Planimeter for Leaves—*Carman*

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The Probability Distribution of Camera Resolution—*Rosenau*

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Spectral Variation of Blackbody Radiation

Marc G. Dreyfus

A simple method is described for calculating the rate of change with temperature of blackbody radiance in a selected narrow spectral region.

Introduction

The purpose of this paper is to describe a convenient rule-of-thumb for estimating the rate of change of blackbody radiance in a narrow spectral region as a function of temperature. This rule will be presented in a relatively simple form that can be committed to memory. It is intended as a supplement to the various published descriptions,[1-4] tables,[5-8] and slide rules[9-12] of blackbody radiation characteristics which are currently available.

Development

The Planck blackbody radiation formula[13] states that:

$$W_\lambda = c_1\lambda^{-5}/(e^{c_2/\lambda T} - 1) \tag{1}$$

where W_λ = spectral radiant emittance at wavelength λ,[14,15]
$c_1 = 2\pi hc^2 = (3.7412 \pm 0.0002) \times 10^{-5}$ erg cm^2/sec,
$c_2 = ch/k = 1.43877 \pm 0.00003$ cm °K.

The quantity we will calculate is

$$\frac{1}{W_\lambda}\frac{dW_\lambda}{dT},$$

which is the fractional change in W_λ per °K change in temperature.

Wien's displacement law states that:

$$\lambda_m T = c_2/\alpha = 0.289776 \pm 0.000006 \text{ cm °K}, \tag{2}$$

where λ_m = wavelength of peak spectral radiant emittance at temperature T and where $\alpha = 4.965114$, which is the value of x maximizing the function $x^5/(e^x - 1)$.

From Eq. (1) above it can be shown[11] that:

$$\left(\frac{1}{W_\lambda}\right)\left(\frac{dW_\lambda}{dT}\right) = \left(\frac{d \log W_\lambda}{dT}\right)_{\lambda \text{ fixed}} = \left(\frac{e^{c_2/\lambda T}}{e^{c_2/\lambda T}-1}\right)\left(\frac{c_2}{\lambda T^2}\right). \tag{3}$$

If we define

$$n = \frac{T}{W_\lambda}\frac{dW\lambda}{dT} \tag{4}$$

and

$$\beta = \lambda/\lambda_m, \tag{5}$$

then it follows, from Eqs. (2) and (5), that

$$\alpha/\beta = c_2/\lambda T = \gamma \tag{6}$$

and, from Eqs. (3), (4), and (6), that:

$$n = \gamma e^\gamma/(e^\gamma - 1), \tag{7}$$

where $\gamma \doteq 5/\beta$,

and

$$(1/W_\lambda)(dW_\lambda/dT) = n/T. \tag{8}$$

Discussion

The quantity n, defined above in Eq. (4), can be heuristically characterized as the exponent in the equation $W_\lambda = KT^n$, where K is a constant, since, in this case,

$$dW_\lambda/dT = nKT^{n-1} \text{ and } \frac{1}{W_\lambda}\frac{dW_\lambda}{dT} = \frac{n}{T}.$$

Another way of viewing the quantity n is that it is equal to the percentage change in W_λ for a 1% change in absolute temperature; this can be seen by recasting Eq. (4) into the form:

$$n = \frac{dW_\lambda}{W_\lambda}\Big/\frac{dT}{T}. \tag{9}$$

It can be shown that the asymptotes of Eq. (7) are $n = \gamma$ for large γ, and $n - 1 = \gamma/2$ for small γ.

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These asymptotic values can be used to approximate n as follows:

$$\begin{aligned} n &\doteq 5/\beta \quad \text{for} \quad \beta \leq 2.5, \\ n - 1 &\doteq 2.5/\beta \quad \text{for} \quad \beta > 2.5. \end{aligned} \tag{10}$$

This approximation is in error by less than 16% in the worst case when $\beta = 2.5$.

Figure 1 is a graph of n vs β computed from both Eqs. (7) and (10). The use of Eq. (10) reduces the estimation of $(1/W_\lambda)\,(dW_\lambda/dT)$ to the scheme shown in Fig. 2. Figure 3 shows the correction factor that should be applied to the approximate value of n computed according to Fig. 2 if a more exact n value is desired.

Applications

Figure 2 can be used to evaluate the temperature sensitivity of radiometric devices, as illustrated by the following two sample problems:

Problem I: A radiometer operating at a wavelength of 10 μ is to be calibrated to an accuracy of 2% with a blackbody used at room temperature (293°K). With what accuracy, ΔT, must the blackbody temperature be known?

Solution: $\lambda_m = \dfrac{2898\ \mu\,°\text{K}}{293°\text{K}} = 9.9\mu,$

$$\beta = \frac{10\mu}{9.9\mu} = 1.0,$$

$$n = \frac{5}{1.0} = \frac{5.0\%\ \text{radiometer signal change for a}}{1\%\ \text{blackbody temperature change.}}$$

$$\therefore \Delta T = \frac{2\%}{5.0\%}\,(0.01 \times 293°\text{K}) = 1.2°\text{K}.$$

Problem II: A two-color radiometer operating at wavelengths of 0.75 μ and 1.5 μ on an incandescent blackbody source with $T = 3000°$K shows a 5% imbalance in the signals from the two monochromatic channels. How much change, ΔT, in source temperature is required to equalize the two channel signals?

Solution: $\lambda_m = \dfrac{2898\ \mu°\text{K}}{3000°\text{K}} = 0.97\ \mu.$

For the 0.75 μ channel: $\beta = \dfrac{0.75\ \mu}{0.97\ \mu} = 0.78$

and $n = \dfrac{5}{0.78} = 6.4.$

For the 1.5 μ channel: $\beta = \dfrac{1.5\ \mu}{0.97\ \mu} = 1.6$

and $n = \dfrac{5}{1.6} = 3.2.$

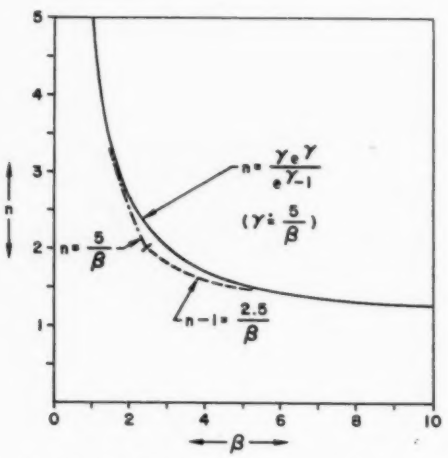

Fig. 1. Graph of n vs β, showing the curve obtained using Eq. (7) (solid line) and the curve obtained using the approximation given in Eq. (10).

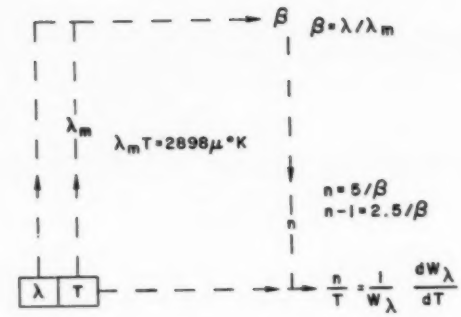

Fig. 2. Scheme for estimating $(1/W_\lambda)\,(dW_\lambda/dT)$.

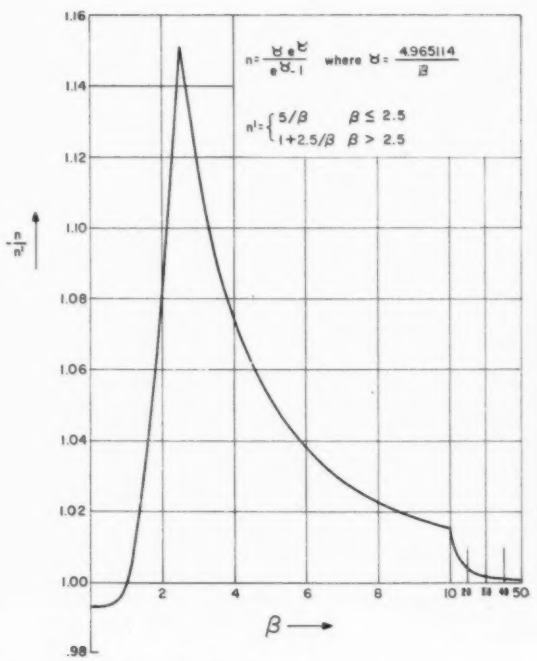

Fig. 3. Correction factor for approximating $n = (dW_\lambda/W_\lambda)/dT/T)$.

$\Delta n = 6.4 - 3.2 = 3.2\%$ change in lamp radiance (or equivalently radiometer balance) for a 1% change in lamp temperature.

$$\Delta T = \frac{5\%}{3.2\%}\,(0.01 \times 3000°\text{K}) = 47°\text{K}.$$

In closing we would like to note that the large values of n generated by short wavelengths (i.e., by small values of β) show that the short-wavelength radiance of a blackbody is extremely sensitive, on a percentage basis, to changes in temperature. Several radiometers[16] have been constructed which use this rapid variation of short-wavelength radiance to good advantage to obtain a sensitive indication of the temperatures of incandescent objects which are relatively independent of variations in surface emissivity.

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photo Jacqueline

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The patents reviewed below have been issued by the U.S. Patent Office on the dates quoted except where otherwise mentioned. The patent number, date of issuance, and classification number are quoted in the first line. The filing date is that of the earliest patent application. The opinions stated in the reviews are those of the reviewers and are not meant to express the thinking either of the organizations with which members of the panel are associated, of the Optical Society of America, or of this journal. Normally, statements of fact are based upon the patents and not independently verified. Printed copies of American patents may be ordered from the Commissioner of Patents, Washington 25, D.C., for 25¢ each. A weekly subscription service to any selected subclass is also available from the Patent Office.

3,051,041 28 Aug. 1962 (Cl. 88-24)
Image projection.
E. H. Lehmann and W. D. Wright. Assigned to Xerox Corporation. Filed 29 May 1959.

This patent describes a projection system for projecting either a transparency or a specularly reflective picture onto a screen. The patent covers the use of the field lens adjacent to the object in order to conserve the size of the condensing lens. The term "field lens" is never used, and the element is considered to have an effect on the projection lens, but not very much. D.E.W.

3,051,054 28 Aug. 1962 (Cl. 88-65)
Light-polarizing articles and method of making same.
H. D. Crandon. Assigned to American Optical Company. Filed 18 Dec. 1958.

A method of making a thin polarizing film bonded to a glass surface is described. The bonding is done by heat; the film is polyvinyl alcohol containing silicic acid. W.L.H.

3,053,135 11 Sept. 1962 (Cl. 88-1)
Refractor for presenting pictures in three-dimensional effect.
N. Tanaka. Filed 9 May 1960.

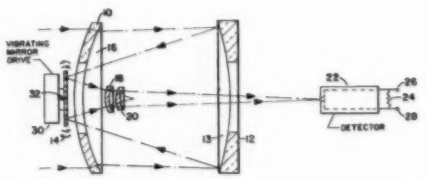
The construction of a transparent screen is described which, when placed a short distance in front of a photograph or transparency, is said to create the illusion of a three-dimensional effect. The screen, or "refractor", consists of two transparent plates, one surface of each having been formed into ridges or waves of about 3-cm pitch and 20° for the maximum sloping angle. The slopes on one of the plates has additional "ripples." The plates are placed with the waves interlocking and with a spacing of about 15 mm. This refractor is placed about 7 cm in front of the picture and viewed from, for example, 1.5 m. It is claimed that the deviation produced by the ripples, being perceived differently by the two eyes, produces the desired effect. D.E.W.

3,053,136 11 Sept. 1962 (Cl. 88-1.5)
Combined range and view finder with different size image fields.
H. Ito and K. Yamaji. Assigned to Canon Camera Company, Inc. Filed 22 Aug. 1957 (in Japan 30 Oct. 1956).

A combination of inverse Galilean optical system in a concave mirror viewer or Albada finder optical system can be interchanged in the principal light path behind a semitransparent mirror. The mirror also serves to bring the range-finding system into the field of view. The field viewed through the inverse Galilean optical system corresponds to an ultrawide-angle objective, whereas the field viewed through the Mark finder optical system corresponds to that of a narrow objective lens. D.E.W.

3,054,899 18 Sept. 1962 (Cl. 250-83.3)
Optical scanning system.
W. B. McKnight and D. E. Holter. Assigned to the U.S.A. as represented by the Secretary of the Army. Filed 24 June 1960

The patent describes a catadioptric system using a Bouwers corrective lens. The plane secondary mirror is vibrated to scan the field of view across the aperture of detector (22). 18 is a collimating lens, probably having aspheric surfaces. Lens 20 is for focusing the image on the detector. D.E.W.

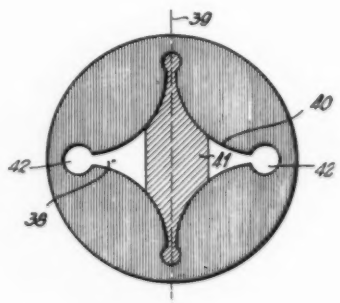


3,055,261 25 Sept. 1962 (Cl. 88-14)
Optical apparatus for curve comparison.
T. H. Braun and R. T. Gerew. Assigned to the Superior Oil Company. Filed 21 Jan. 1959.

Optical apparatus for measuring the longitudinal displacement of micrologs used in oil-well logging. The two optical systems are interconnected so that comparisons of two curves can be made with the third. The mirror systems are arranged so that focus is maintained irrespective of the position of the measuring drum. D.E.W.

3,055,263 25 Sept. 1962 (Cl. 88-14)
Optical apparatus for determining the position of an object.
C. Kuehne. Assigned to Askania-Werke. Filed 15 June 1959 (in Germany 14 June 1958).

This patent is concerned only with the sensitivity of photoelectric devices for locating the position of a line on a graduated scale or circle. The problem is created due to the nonuniformity in the width of such lines, which causes a variation in sensitivity of the detection apparatus. The problem is analyzed mathematically, and it is shown that an exponential mask produces the desired result. In the figure, the line whose position is to be determined is imaged on an aperture whose quadrants, 40, have the required shape. D.E.W.



3,056,696 2 Oct. 1962 (Cl. 117-211)
Ultrathin films.
C. M. Browne. Assigned to Libbey-Owens-Ford Glass Company. Filed 4 June 1958.

This patent describes a process for the deposition of thin films to glass for the purpose of achieving electrical conduction and/or control and selection of light transmission. A particular feature is a technique for coating specified areas by use of a special masking coating on adjacent areas. A.E.M.

continued on page 1163

Computed Transmission Spectra for 2.7-Micron H_2O Band

David M. Gates, Robert F. Calfee, and David W. Hansen

The spectral line positions, strengths, and half-widths of the ν_1, $2\nu_2$, and ν_3 bands of the 2.7-μ region of absorption for water vapor have been computed and checked against laboratory spectra for the range 2857 to 4444 cm^{-1}. From a knowledge of these lines theoretical transmission spectra at infinite spectral resolution at a given pressure, temperature, and water vapor concentration have been determined. From the theoretical transmission spectra certain degraded spectra for finite slit-width are computed, and a comparison is made with a high-altitude atmospheric absorption spectrum of solar radiation.

Introduction

It has been evident for many years that the only fundamental approach to atmospheric transmission problems at infrared frequencies would be through an understanding of the complete detailed spectrum, band for band and line for line. However, the enormous complexity of this procedure has deterred many investigators from this approach. The problem is further complicated by the fact that the strength (intensity) and half-width of each line are dependent upon temperature and pressure as well as dependent upon the concentration of the absorbing gas. Faced with the need to compare various spectroscopic observations of atmospheric transmission at infrared frequencies, both at low resolution and at high resolution, it became evident that one had to tackle the problem of computing the positions, strengths, and half-widths of all the spectral lines within any region of the spectrum. From this knowledge of the lines, it would be possible, at least in principle, to compute the integrated effect of all these lines on the transmission at any given position in the spectrum.

The two absorbing constituents which are of greatest importance for atmospheric transmission problems in the infrared region of the spectrum are water vapor and carbon dioxide. It was decided to work with water vapor first and to analyze the broad absorption region around 2.7 μ, which involves the bands ν_3, ν_1, and $2\nu_2$. The many excellent experimental observations and analyses which have now been made of the water vapor spectrum, coupled with computations of line-width and intensity, make it possible to undertake systematically such a program. Furthermore, the advent of the large computer makes the task of computing the transmission for given atmospheric conditions a manageable problem.

The water vapor molecule possesses a very complicated spectrum with irregularly spaced lines. It is triatomic, has three normal modes of vibration and possesses three very different moments of inertia, hence falling into the category known as asymmetric top rotators. The general theory concerning such a molecule is to be found fully discussed by Herzberg.[1] The analytical formulation of the rotational structure of H_2O is well known[2-4] and will not be repeated here.

The strong broad absorption region around 2.7 μ is caused by the following vibrations: ν_3, a strong stretching fundamental with the change of dipole moment during the vibration along the least axis of inertia, giving rise to a type A band with the origin at 3755.92 cm^{-1}; ν_1, a weaker stretching fundamental with the change of dipole moment along the intermediate axis of inertia (type B band), with the origin of 3657.08 cm^{-1}; and $2\nu_2$, the first overtone of the bending fundamental (type B band) with the band origin at 3151.60 cm^{-1}. The relative intensities of these bands are approximately $\nu_3:\nu_1:2\nu_2 = 120:12:1$. In addition there are lines due to bands of isotopic configurations of H_2O whose normal abundances are: H_2O^{18}, 0.20 %; H_2O^{17}, 0.037 %; and HDO, 0.027 %. Lines are also due to bands in which the lower level is vibrationally excited. At atmospheric temperatures, <320°K, the only such level which must be considered is the lowest, ν_2, and its abundance is very small, 0.033 % at 287°K.

A report by Gates *et al.*[5] lists in order of frequency approximately 4458 lines within the frequency span 2857 cm^{-1} to 4444 cm^{-1} giving their position, intensity,

The authors are with the National Bureau of Standards, Boulder, Colorado.

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half-width, rotational identification for upper and lower states, energy of the lower state, rotational transition strength, and band designation. The energy levels, on which the line positions were based, were derived in turn from observed line positions. All lines observed either in the atmospheric absorption of solar radiation or in laboratory spectra, with the exception of a few very weak lines, were accounted for. It is possible to predict weaker lines that have not been observed due to insufficient resolving power under the proper conditions. The occurrence of these very weak lines are discussed in the report. The quantum mechanics of the asymmetric top rotator, upon which the line strengths and half-widths of the lines were based, is also given in the report. The line strengths and the half-widths as given in the report are believed to be sufficiently correct for absorption computations. Line strengths were calculated at 287.7°K for all possible transitions in the three principal bands up to $J_{max} = 15$. The strengths are based on absolute measurements from laboratory and atmospheric spectra. The strongest line (404–503 in ν_3, at 3838 cm^{-1}) has $S = 9.23 \times 10^3$ $cm^{-1}/g\text{-}cm^{-2}$. Since the purpose of the table in the report is to list all lines of possible significance in atmospheric transmission problems, the lower limit of S was set at 10^{-3} $cm^{-1}/g\text{-}cm^{-2}$ in the band wings and at 10^{-2} in the central region 3503 to 3950 cm^{-1}, which includes all lines with $S > 2 \times 10^2$. In addition, weak lines were excluded if within 0.25 cm^{-1} of a strong line whose strength exceeded the strength of the weak line by 10^3 or if within 0.5 cm^{-1} of a strong line whose strength exceeded the strength of the weak line by 4×10^3. This limitation excluded from the table of the report a large proportion of the lines in the weak branches of the original bands and in the weak satellite bands due to H_2O^{18}, H_2O^{17}, and the "hot" transitions 011 to 010, 110 to 010, 030 to 010. No attempt was made to list lines in the ν_3 band of HDO ($\nu_0 = 3704.25$ cm^{-1}), since it was determined that its strongest lines, with few exceptions, would be excluded by the above criteria. The very weak combination bands of HDO, $\nu_1 + \nu_2$ ($\nu_0 = 4100.05$ cm^{-1}), and $3\nu_2$($\nu_0 = 4145.59$ cm^{-1}), also are not considered.

It must be emphasized that the exclusion of extremely weak lines from the report was for purposes of saving space in printing and time in transmission computations based on line-by-line integrations. The actual distribution in strength of the lines in the spectrum includes additional weak lines in the categories mentioned and other weaker lines of vibrational and rotational states which have not been included here. These higher-state lines are important when considering the absorptivity or emissivity of water vapor at elevated temperatures.

Transmission Calculations

In order to compute the transmission of the atmosphere to infrared radiation in the wavelength regions of the water vapor absorption bands, it is necessary to take into account each and every significant line in the spectrum and to compute the collective effect of many lines on the transmission at any specific frequency. The precise nature of an observed spectrum will depend upon the instrument used for the observation, the spectrum being degraded by the influence of the slit or instrument factor. Before a careful analysis can be made of the spectral transmission as observed under various conditions, it is first necessary to establish in detail the theoretical spectral transmission which would be recorded with an instrument of infinite resolving power. The procedure for doing this will first be described and then the method used for computing the degraded spectra will be discussed.

As is well known, the monochromatic transmission at a frequency ν of m g-cm^{-2} of absorbing gas at a constant pressure and temperature, is

$$T_\nu(m) = \exp(-k_\nu m), \tag{1}$$

where k_ν is the monochromatic absorption coefficient.

Each absorption line shape is affected by collisions which shorten the natural lifetime of excited vibrational states. The following Lorentz formula is taken to represent reasonably the spectral line shape which gives the monochromatic absorption coefficient in the following form:

$$k_\nu = \frac{S}{\pi}\frac{\alpha}{[(\nu - \nu_0)^2 + \alpha^2]}, \tag{2}$$

where ν_0 is the frequency of the line center, S is the line strength which depends upon temperature according to

$$S = S_0\left(\frac{T_0}{T}\right)^{3/2}\left[\exp\frac{-E''}{k}\left(\frac{T_0 - T}{T\,T_0}\right)\right], \tag{3}$$

α is the half-width of the line which depends upon pressure and temperature in the following manner:

$$\alpha = \alpha_0\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)^n, \tag{4}$$

where P is the total pressure of the gas, T is the absolute temperature, and n depends upon the nature of the broadening gas and the frequency of the transition. For N_2–H_2O collisions, Benedict and Kaplan[6] show $n = 0.62$ to be a good representative value.

However, the transmission at any frequency in the spectrum depends not only on the shape, half-width, and strength of the nearest line, but is also influenced by the wings of dozens of lines on either side. Therefore, to get the actual absorption coefficient at any frequency, it is necessary to sum the influence of many lines as follows:

$$k(\nu) = \sum_{\nu_0} k_\nu = \sum_{\nu_0} \frac{S_{\nu_0}}{\pi} \frac{\alpha}{(\nu - \nu_0)^2 + \alpha^2}. \quad (5)$$

The transmission for a given pressure, temperature, and water vapor concentration is now given as

$$T(\nu) = \exp(-k(\nu)m). \quad (6)$$

The total absorption across an entire band is invariant to the spectral slit-width of the instrument (Nielsen *et al.*[7]). For this reason the total band absorption, rather than the specific absorption within a narrow spectral interval, is often given by experimentalists. The total band absorption is given by

$$A = \int_{\nu_1}^{\nu_2} A(\nu)d\nu = \int_{\nu_1}^{\nu_2} [1 - T(\nu)]d\nu, \quad (7)$$

where ν_1 and ν_2 are the frequency limits for the band.

Computational Procedure

It was desired to compute the transmission as a function of the frequency across a definite frequency interval for a given pressure, temperature, and water vapor concentration. To avoid any end effects, the computation was extended to include the strong lines 150 cm^{-1} beyond either side of the interval selected. Starting with the first point of the interval, the transmission was computed by calculating directly the contributions of all lines by means of the Lorentz line shape formula. This was a straight sum of the k_ν's at this position. The frequency value was then increased by a fixed increment, 0.01 cm^{-1}, and the transmission again calculated. When the point came within 0.05 cm^{-1} of a line center, the increment was decreased to 0.0005 cm^{-1} in order to gain the full influence of the line on the calculations. Furthermore, at the position of each line the influence of all other lines was summed up to give an added effective strength to the single line absorption coefficient. By using a coarse increment when far from line centers and a fine increment when close, a marked saving of computer time was realized. After calculating the transmissions throughout the total interval, the total absorption was calculated using Simpson's rule, taking into account the two sizes of step intervals.

The necessary data for computation are the pressure in atmospheres, the water vapor concentration in precipitable centimeters, and the absolute temperature along with the line positions, line strengths, half-widths, and ground-state energy values. The computed theoretical water vapor spectra for the frequency interval 3800 to 3900 cm^{-1} are shown in Figs. 1 and 2 for a pressure of 0.1 and 1.0 atm, respectively at two concentrations of water vapor 0.001 and 0.01 cm of precipitable water in the path for a temperature of 287.7°K.

Degraded Spectra

A spectrometer scanning an absorption spectrum will not record it with the sharp detail of the natural line shape but will degrade the spectrum because of finite slit-widths and limited dispersion of the grating or prism. Since all observed spectra are of this degraded nature to various degrees, it is desirable to modify the theoretical spectrum described earlier with a slit function or instrument factor. Several authors have discussed slit factors including Nielsen *et al.*,[7] Dennison,[8] Kostkowski and Bass,[9] and Rautian.[10]

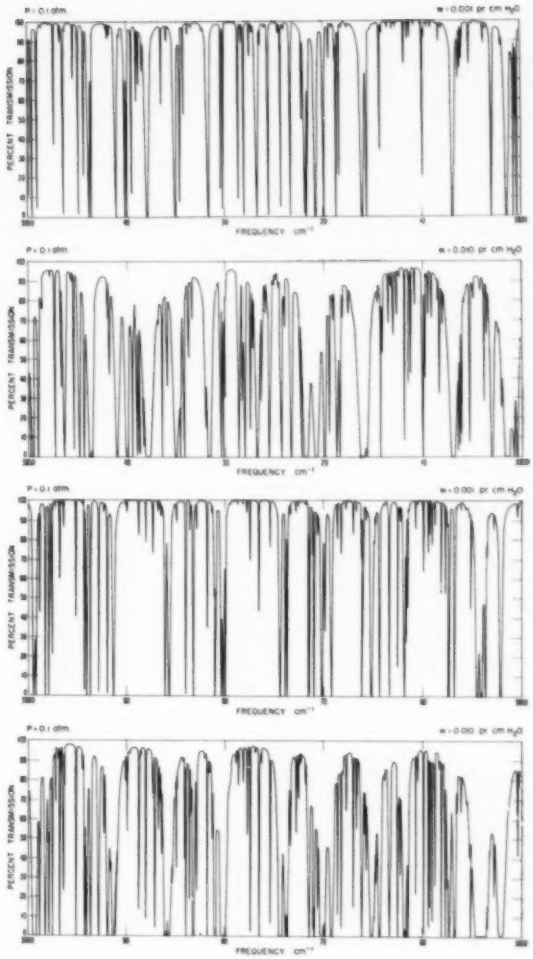

Fig. 1. Computed theoretical water vapor transmission spectra for the frequency range 3800 to 3900 cm^{-1} at 0.1 atm pressure.

The slit function, $\rho(\nu)$, is defined according to the degraded transmission $\bar{T}_{\nu_i}$ recorded by the spectrometer at a frequency ν_i as follows:

$$\bar{T}_{\nu_i} = \frac{\int_{\nu_i - a}^{\nu_i + a} \rho(\nu) T_\nu d\nu}{\int_{\nu_i - a}^{\nu_i + a} \rho(\nu) d\nu}, \quad (8)$$

where T_ν is the theoretical transmission at infinite resolving power at any frequency ν, and ν_i is the frequency

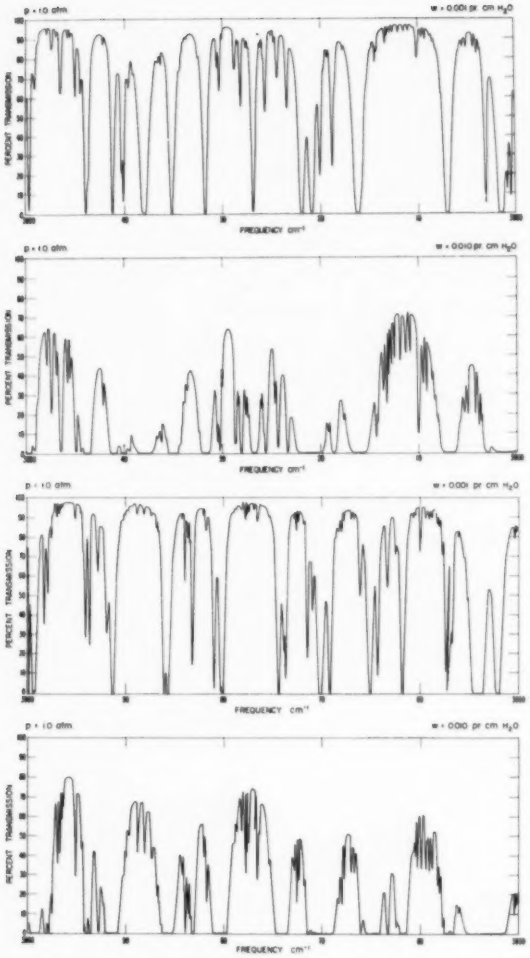

Fig. 2. Computed theoretical water vapor transmission spectra for the frequency range 3800 to 3900 cm^{-1} at 1.0 atm pressure.

at the center of the spectral interval being momentarily scanned by the exit slit, and a is the spectral slit-width (defined as one-half of the total frequency span passed by the spectrometer slits).

Various approximations to the slit function can be derived, such as a Gaussian distribution, a trapezoidal type of distribution, and a triangular function. The simplicity of the triangular function and the fact that it represents reasonably well the slit distortions across the central maximum make it attractive for computational purposes. The triangular slit function was given the following form:

$$\rho(\nu) = a - |\nu - \nu_i|. \tag{9}$$

To compute the degraded spectrum from the theoretical spectrum, the triangular slit function was superimposed upon the theoretical spectrum. Then, the average transmission was calculated across the frequency span passed by the slit. The slit function was shifted across the spectrum by increments of approximately 0.2 to 0.4 cm^{-1} depending upon the slit-width used, and at each position the average transmission across the slit was computed, using Eq. (8). The averaging process within the spectral interval was calculated in steps of 0.05 cm^{-1}.

The theoretical water vapor spectra of Fig. 1 covering the frequency range 3800 to 3900 cm^{-1} are shown in degraded form in Figs. 3–5. The degraded spectra were calculated for spectral slit half-widths of 0.5 cm^{-1} and 1.0 cm^{-1}, or a full slit span of 1.0 cm^{-1} and

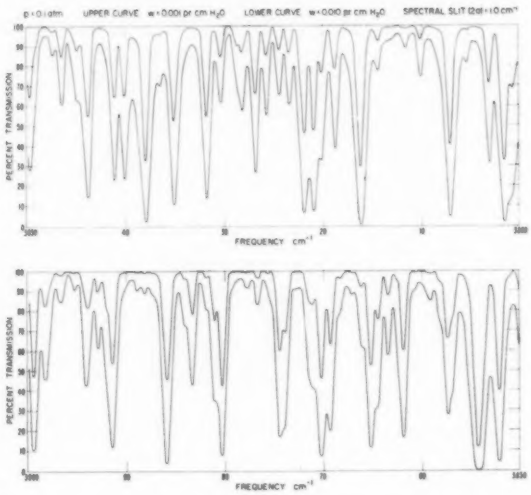
p = 0.1 atm
UPPER CURVE w = 0.001 pr cm H2O
LOWER CURVE w = 0.010 pr cm H2O
SPECTRAL SLIT (2a) = 1.0 cm-1
PERCENT TRANSMISSION
FREQUENCY cm-1

Fig. 3. Computed degraded water vapor transmission spectra for the frequency range 3800 to 3900 cm^{-1} at 0.1 atm pressure and a full spectral slit-width (triangular) span of 1.0 cm^{-1}.

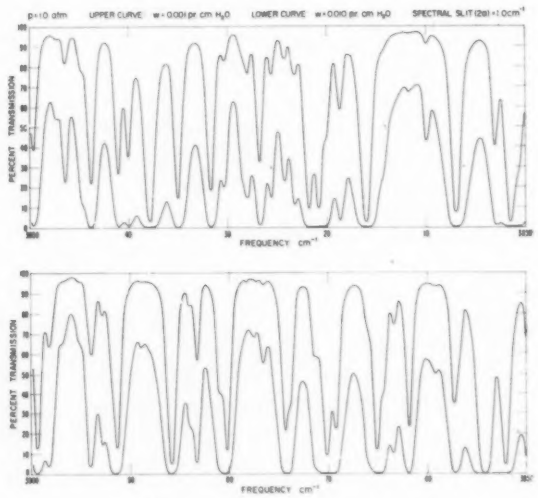
p = 1.0 atm
UPPER CURVE w = 0.001 pr cm H2O
LOWER CURVE w = 0.010 pr cm H2O
SPECTRAL SLIT (2a) = 1.0 cm-1
PERCENT TRANSMISSION
FREQUENCY cm-1

Fig. 4. Computed degraded water vapor transmission spectra for the frequency range 3800 to 3900 cm^{-1} at 1.0 atm pressure and a full spectral slit-width (triangular) span of 1.0 cm^{-1}.

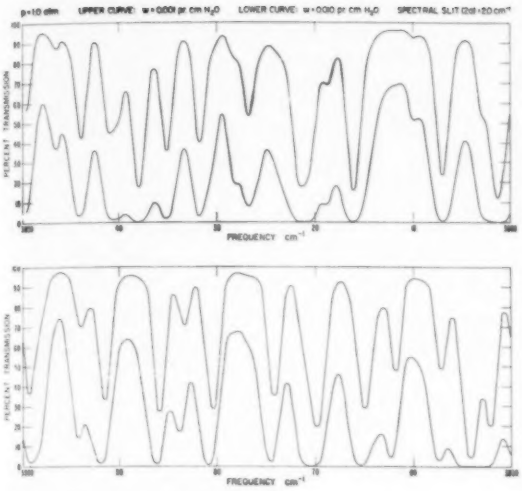

Fig. 5. Computed degraded water vapor transmission spectra for the frequency range 3800 to 3900 cm^{-1} at 1.0 atm pressure and a full spectral slit-width (triangular) span of 2.0 cm^{-1}.

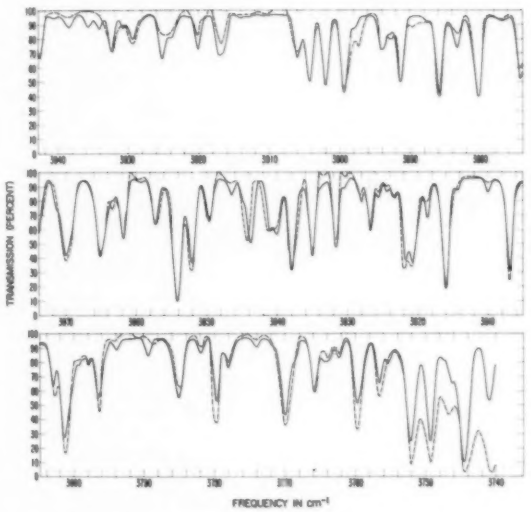

Fig. 6. Comparison between a computed degraded spectrum and an observed spectrum taken with the sun as a source from an aircraft at an altitude of 13.7 km over Florida. Dashed curve: spectrum taken from CARDE aircraft at 0830 on 16 November 1962, zenith angle 71°, altitude 13.7 km. Solid curve: computer calculated spectrum for p = 0.0691 atm, w = 0.0030 pr. cm H_2O, T = 217°K, slit 1.75 cm^{-1}.

2.0 cm^{-1}. Inspection of these figures will show the influence of slit-width, pressure, and water vapor concentration on the observable spectra. Many more examples of these degraded water vapor spectra are contained in an atlas by Gates *et al.*[11]

Comparison with Observed Spectra

Cumming *et al.*,[12] at the Canadian Armament Research and Development Establishment, have recorded the solar and atmospheric absorption spectrum from an altitude of 13.7 km above Florida on 16 November 1962 at 0830 h (zenith angle 71°) for the 2.7-μ wavelength region. This observed spectrum was reduced to a plot of transmission vs frequency in cm^{-1}, and a degraded spectrum was computed using a full slit-width of 1.75 cm^{-1} (a = 0.875 cm^{-1}). Several water vapor concentrations were tried until a good correspondence between the calculated and the observed spectrum was achieved. The best fit occurred with a water vapor concentration of 0.003 precipitable centimeters along the slant path and a pressure of 0.0691 atm. The pressure used is not the pressure at 13.7 km altitude but half the pressure at this altitude. The temperature used was 217°K which reasonably represented the temperature along the observed path.

Figure 6 shows a comparison of a reconstructed high-altitude observed spectrum and the degraded computed spectrum over the frequency range 3740 to 3940 cm^{-1} in the high-frequency wing of the 2.7-μ band. Since the computed spectrum is for water vapor only, there is a difference in the two curves in the region nearest the center of the band where the influence of CO_2 becomes significant. From the CARDE spectrogram it was difficult to establish the absolute value of the transmission in some of the narrow windows between the lines, and hence at several positions throughout the spectrum the observed transmission is shown to be 100 %. The transmission at these positions should probably be reduced to agree with the calculated spectrum. Nevertheless, Fig. 6 is an illustration of the fact that the observed spectrum can be calculated with precision in all its detail when the proper values of the parameters involved are used.

The authors particularly wish to thank W. S. Benedict of The Johns Hopkins University and the National Bureau of Standards, Washington, D.C., for his advice and assistance concerning the details of the computed theoretical spectrum.

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Six-Meter Focal Length Ebert-Type Infrared Spectrograph. Part I. Details of the Spectrograph

K. Narahari Rao and Harald H. Nielsen

A description is presented of a recently constructed Ebert-type vacuum infrared spectrograph. The grating employed is a 73.25 grooves per mm 25.4 × 12.7 cm ruled echelle blazed for an angle of 63° 26′. The entire instrument operates in a vacuum. Facilities have been provided to use the spectrograph with tritium-substituted compounds, such as NT_3, TF, CT_4, etc.

I. Introduction

One of the most extensively studied problems in the infrared region of the electromagnetic spectrum pertains to the observation, measurement, and analysis of the absorption spectra of small polyatomic molecules. The vibration–rotation bands of these molecules occur in different parts of the near infrared spectrum. For instance, if it is desired to investigate the structure of the ammonia molecule from observations on its infrared spectrum, it is important to be able to study as many bands of this molecule as possible. The various vibration–rotation bands of ammonia occur almost throughout the region of 1–20 μ. In order to use these data effectively it is necessary to obtain internally consistent spectral positions for the rotational structure of all these bands. Furthermore, the interpretation of infrared spectra of polyatomic molecules is in itself a time-consuming and involved problem. Therefore, it is imperative to devise the infrared techniques with a view to obtaining observational data as speedily as possible without sacrificing much of the spectral resolution and precision of measurements. Until recently, it had been customary to observe infrared absorption spectra in the first order of a grating. This procedure requires the use of at least four gratings with different groove spacings in each, in order to cover the spectral region from 1 to 20 μ where most of the vibration–rotation bands of small polyatomic molecules occur. As a result of this use of different gratings, and also due to the unavailability of an adequate number of infrared standards, there has frequently been difficulty in obtaining internally consistent data for the spectral positions of the rotational lines in different vibration–rotation bands. Rao *et al.*[1] demonstrated the advantages of employing a coarse grating, such as one with 40 grooves per mm, mounted in echelle fashion and used in higher spectral orders for obtaining observations in the entire region of 1–40 μ. Excellent ruled echelles are now available as a result of the efforts of George Harrison and colleagues at the Massachusetts Institute of Technology. Harrison has presented extensive discussions of echelle spectroscopy in two recent articles.[2,3] Also, nowadays there are available superior photoconductive detectors for use in the near infrared region between 1 and 6 μ. The spectrograph described in this article utilizes these modern gratings and detectors.

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II. Details of the Spectrograph

The Ebert monochromator has been the subject of numerous recently published papers,[4–10] and, therefore, there is no need to go into the details of the advantages in this type of mounting.

A. The Basic Optics

The schematic arrangement of the optics shown in Fig. 1 pertains to the present instrument. The entrance and exit slits, S_1 and S_2, are curved, each slit having a radius of curvature of about 12.5 cm. The grating is a 25.4 × 12.7 cm ruled echelle with 73.25 grooves per mm on its surface and blazed for an angle of 63°26′. It is a Bausch & Lomb replica copied from the original which has been ruled by Harrison at the Massachusetts Institute of Technology. The concave mirror which acts both as a collimator and a telescope has a focal length of nearly 6.4 m and a diameter of about 63.5 cm. The photographs shown in Figs. 2 and 3

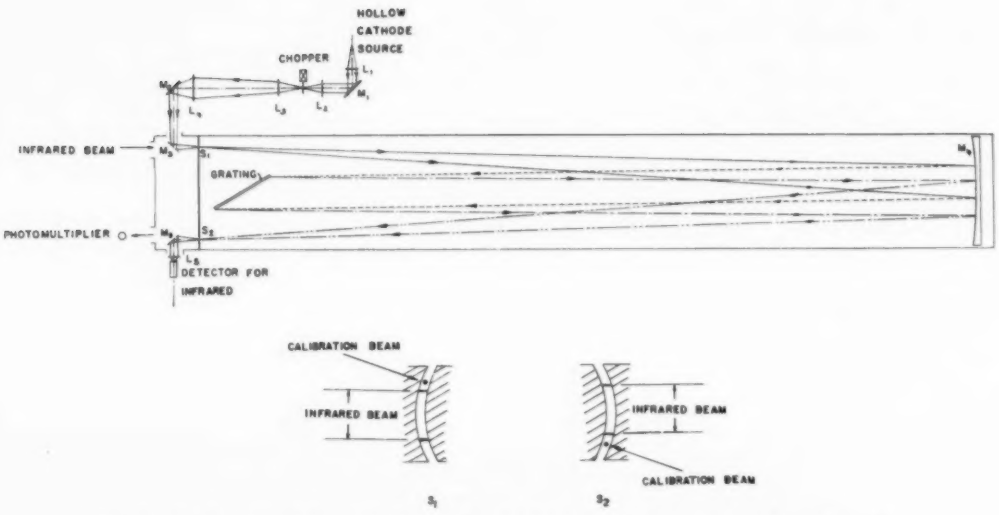

Fig. 1. A schematic of the optics for the 6-m focal length Ebert-type infrared spectrograph.

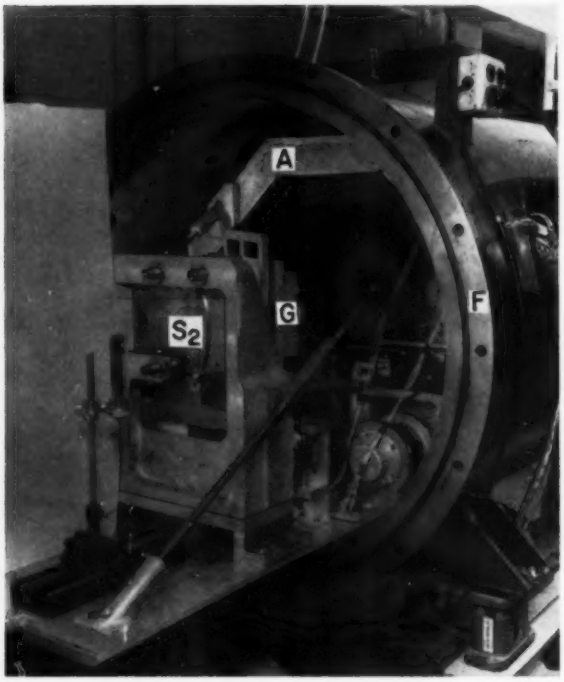

Fig. 2. A view of the grating end of the Ebert-type infrared spectrograph. A—the frame on which the spectrograph optics are installed; F—flange welded to the long steel pipe housing the spectrograph; G—grating; S_2—exit slit.

Fig. 3. A view of the 63.5-cm diam, 6.4-m focal length Ebert mirror. C—end cap rolled away to enable the reaching of the mirror for making adjustments.

present views of the grating, exit slit, and the Ebert mirror.

B. Spectrograph Housing

The optical and mechanical parts of the main spectrograph have been installed on a frame constructed of 3.2 mm thick aluminum sheets around five aluminum octagonal rims. Figure 4 shows a photograph of this structure which has been designed to prevent flexure and twisting. Also, this frame is constructed so that it could be brought into the laboratory in sections and then assembled in the laboratory. This frame

which is nearly 5.5 m in length has been inserted inside a 91-cm diam, 6.1 m long steel pipe. At the two ends of the pipe, flanges with O-ring grooves cut in them have been welded. One of these flanges is shown in Fig. 2. Caps at the two ends can be rolled into position to seal the tube for evacuation. Figure 3 shows a section of this end cap rolled away for making adjustments on the Ebert mirror. The aluminum frame is supported on three knife edge supports. Two of these supports are located at the mirror end, and the third one under the grating section of the optics. The steel pipe rests on vibration flex mountings which have been placed on a base constructed out of $5 \times 5 \times 0.6$ cm steel angle. These precautions have been taken to minimize external vibrations from interfering with the spectrograph optics. Both the interior and the exterior of the steel tube are coated with glyptol.

C. Optics External to the Spectrograph

As indicated in Fig. 1, the optics external to the spectrograph comprises two sections. One of these provides the infrared beam, and the other a calibration beam.

1. Infrared Optics

The infrared section consists of a source of continuous radiation, a monochromator, which is essentially a 60° NaCl prism (17.8 cm base × 14 cm height) with a standard Littrow-type mirror behind it to scan the spectrum. This predispersed beam is then reflected from two concave and four flat mirrors before it arrives at the entrance slit of the grating section. These mirrors have been mounted in various steel boxes supported on steel tables fabricated from angle iron. In each of these boxes an aluminum bed plate resting on three point supports has been installed. The mirrors themselves have been mounted on the bed plates. This type of isolation of the optics from the outside chambers eliminates distortion in the optical beam when the instrument is evacuated. The path length of nearly 11 m between the foreprism and the entrance slit of the grating spectrograph can be used for studying the absorption spectra of noncorrosive gases available in cylinders. For the study of the high resolution spectra of tritium-substituted compounds, the absorption cell containing these compounds has been placed either between the foreprism and the entrance slit of the grating section or behind the exit slit of the spectrograph. It has been found desirable to avoid the intense heat from the source of continuous radiation directly illuminating the absorption cell with tritium-substituted gas in it. As a precautionary measure, an appropriate protective chamber equipped with infrared transmitting windows has been constructed around these cells containing the radioactive samples.

2. Calibration Optics

Radiation from a hollow cathode tube with neon as carrier gas illuminates a small portion of the entrance slit of the grating spectrograph just above the infrared beam (Fig. 1). After passing through the spectrograph it is detected by a 1P21 photomultiplier. The atomic lines emitted in the hollow cathode discharge tube serve as wavenumber markers on the infrared spectrum. Use of long focal length optics along with coarse echelle-type gratings facilitate the calibration procedures. In this type of setup, one can use wider physical slits which would allow more light to pass through the instrument from the hollow cathode calibration source, thereby resulting in the observation of many atomic lines in higher spectral orders. Details of the calibration techniques employed will be discussed in Part II.

D. Grating Drive

The table on which the grating is mounted is connected to an arm with a length of nearly 60 cm. A small steel ball has been installed at the end of this arm. The ball rests upon a fused-quartz optical flat attached to a precision screw. It is a right-hand screw with 26.7-cm travel, 1-mm pitch, 1-mm lead, and was supplied by David Mann & Company, Lincoln, Massachusetts. The contact block is shaped in the form of a right triangle, and the ball rides on the hypotenuse to which the optical flat has been firmly attached. A 15.2-cm diam, 200-teeth worm wheel is mounted on the end of the screw with an associated worm connected to a synchronous motor.

E. The Detector Section

The infrared beam emanating from the exit slit is brought outside the steel pipe by means of a flat mirror and then focused upon an infrared detector. Thus far, lead sulfide and lead selenide detectors cooled to liquid nitrogen temperature have been employed. These enabled the observation of infrared spectra between 1 and 6 μ. In view of the use of a coarse echelle along with a salt foreprism, the spectrograph can, in principle, be employed in the entire region between 1 and 15 μ by changing detectors.

An over-all view of the spectrograph is shown in Fig. 5.

III. Performance of the Spectrograph

The spectrograph is currently used in a single-pass arrangement. Figure 6 shows tracings of portions of the ν_3 band of methane and the $2\nu_1$ band of nitrous oxide. It has been possible to resolve lines separated by 0.05 cm^{-1} in the region between 1 and 6 μ. It may be mentioned that this spectral resolution has been accomplished after using 20 reflections on mirror surfaces and 6 windows of calcium fluoride in the optical path. This resolving power has been maintained in day-to-day

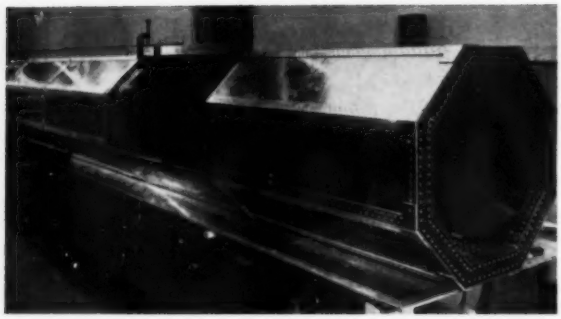

Fig. 4. The octagonal aluminum frame to the ends of which the spectrograph optics have been mounted. The entire frame has been riveted together. The above photograph was taken during the construction of the frame.

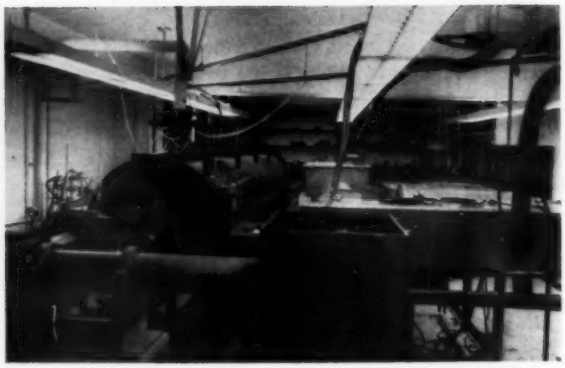

Fig. 5. An over-all view of the Ebert-type infrared spectrograph.

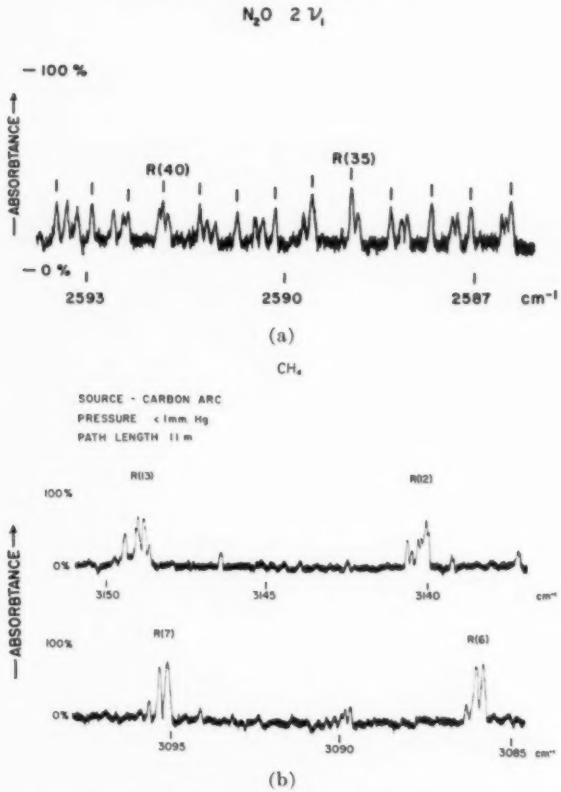

Fig. 6. (a) $2\nu_1$ of N_2O. Detector employed: a PbSe cell, cooled to liquid nitrogen temperature, and supplied by the Santa Barbara Research Center, Goleta, California. (b) CH_4. A few R groups of the ν_3 band of methane. Detector employed: a PbS cell cooled to liquid nitrogen temperature, and supplied by the Infrared Industries Inc., Waltham, Mass. In obtaining the above records of N_2O and CH_4, a 450 cps, Baird-Atomic, Inc., phase-sensitive amplifier has been used in conjunction with the above detectors. The methane data compare excellently with those obtained at the National Bureau of Standards, Washington, D.C.[11]

observations of infrared data, provided the performance of the detector remained the same. In the near future, the spectrograph will be realigned for using the grating in a double-pass arrangement. Details of this work will be reported in a subsequent paper.

In this major undertaking, many individuals and organizations have contributed significantly. The grating and the precision screw have been purchased with the help of funds provided by the National Science Foundation, and some of the parts have been fabricated with the support of the Atomic Energy Commission. We wish to express our thanks for these grants made through The Ohio State University Research Foundation. Robert Hawkins, Robert Merrithew, Phillip Fraley, and Morris Weinberg have all contributed toward the successful completion of this project.

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Six-Meter Focal Length Ebert-Type Infrared Spectrograph. Part II. Precision of Measurements

K. Narahari Rao and Phillip E. Fraley

A semi-empirical procedure for determining spectral positions to an accuracy of ± 0.005 cm^{-1} in the near infrared region is discussed. The infrared spectra have been scanned by rotating the grating with the help of a precision screw. It is believed that the techniques discussed enable the measurement, with the above precision, of many infrared lines in one day.

I. Introduction

In Part I,[1] a general description was presented of the newly constructed Ebert-type infrared spectrograph of this laboratory. The objective of the present paper is to describe some of the calibration procedures that have been adopted with this spectrograph for determining spectral positions in the region 1–6 μ.

It is known that, in regions where photographic techniques can be employed, it is possible to record both the unknown spectrum as well as the standards upon a photographic plate, and the wavelengths of the spectral lines can then be determined by interpolation between standards. However, in the infrared region, the scanning of the spectra is accomplished by rotating the grating. Therefore, the accuracy of the data recorded depends, to some extent, upon the smoothness and precision of the mechanical drive which rotates the grating. In the present spectrograph, a precision screw has been employed to guide the rotation of the grating, and a semi-empirical procedure has been developed for determining the spectral positions speedily.

II. Experimental Details

The basic calibration techniques are essentially those already reported.[2–4] The infrared radiation illuminates the central portion of the entrance slit, and light from a hollow-cathode source is passed through the upper part of the slit slightly above the infrared radiation (see Fig. 1 of Part I). After dispersion, these two beams of radiation are focused on appropriate detectors, and the signals are amplified and recorded on the two pens of a double-pen recorder.

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At this stage, it is convenient to adopt some terms. The two beams of radiation passing through the spectrograph will be called the "infrared beam" and the "calibration beam", and the corresponding traces on the recorder will be called the "infrared spectrum" and the "calibration spectrum". The differences on the wavenumber scales in the infrared and calibration spectra are due to the physical separation of the two pens in the recorder, time constants of the amplifiers, and differences in the optical paths of the two beams of radiation. For a particular position on the chart, if ν_2 is the wavenumber as determined from the "calibration spectra", the unknown wavenumber ν_1 of the "infrared spectra" at the same position on the chart can be obtained if $K = \nu_1/\nu_2$ is determined, where K will be called the "multiplication factor". K can be determined by recording the vibration–rotation bands of the CO molecule as "infrared spectra". As pointed out before by Rao *et al.*,[4] the factor K is not a constant for different angular positions of the grating; however, the variation of K with ν can be determined by making observations on the CO spectra wherever available.

The grating is turned by a lever arm with a round end resting on a flat surface which is driven by a precision screw. The details of this grating drive are shown in Fig. 1. The angle of the flat surface is such that the grating is turned approximately in proportion to sin θ, where θ is the angle that the normal to the grating makes with the Ebert mirror axis. The grating equation is

$$n\lambda = k \sin \theta$$

where k is a constant which depends on the distance between grating grooves and the angle at which the collimated beam strikes the grating with respect to the Ebert mirror axis.

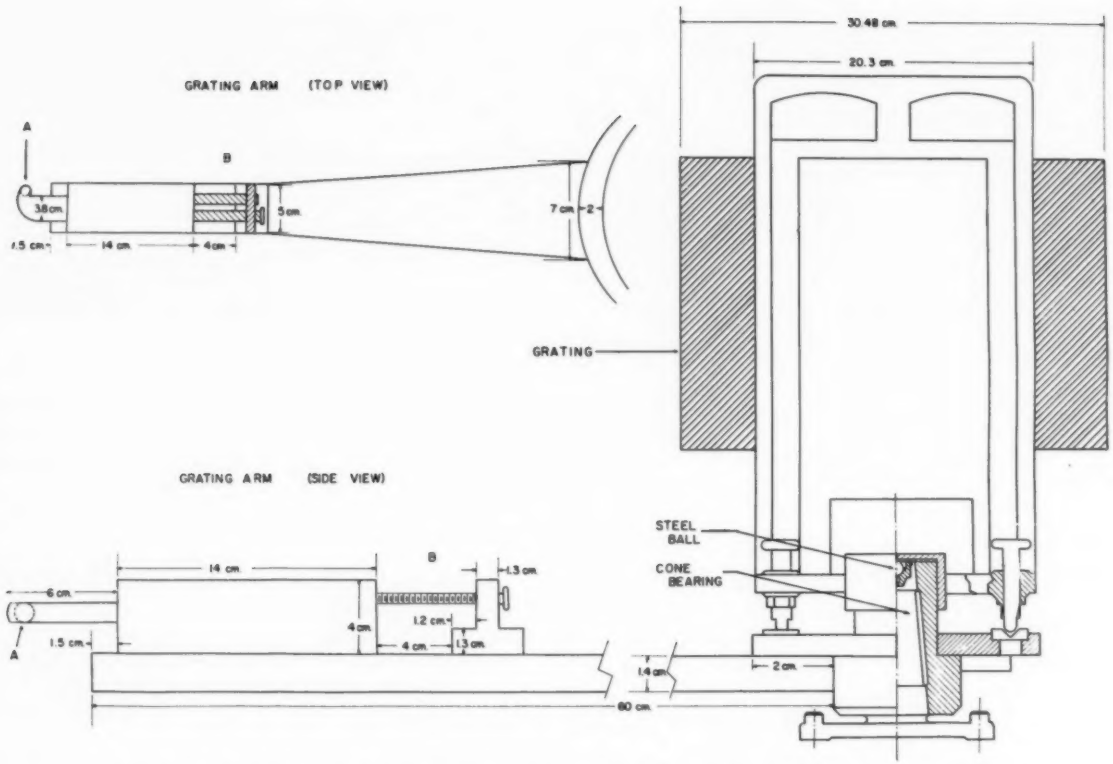

Fig. 1(a). Details of the grating drive employed with the Ebert-type infrared spectrograph.

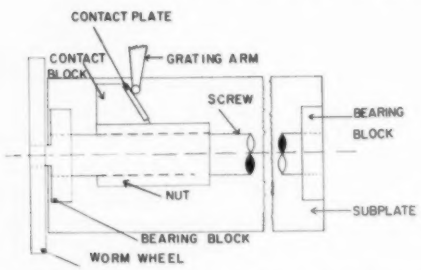

Fig. 1(b). Contact block attached to the precision screw.

If

$$\frac{d(\sin\theta)}{dt} = \frac{n}{k}\frac{d\lambda}{dt}$$

is a constant and the speed of the chart paper is a constant, then $\Delta\lambda$, the difference in wavelength between two spectral lines, is proportional to the distance measured between the lines on the chart paper. Therefore, linear interpolations between wavelengths should be valid.

It has been found that the drive is not exactly linear with respect to λ, but that $\Delta l/\Delta\lambda$ must include a correction term which is linear with respect to λ. The equation to be used may be written as

$$\frac{\Delta l}{\Delta\lambda} = A + 2B\lambda. \tag{1}$$

Equation (1), when integrated, gives

$$l = l_0 + A\lambda + B\lambda^2, \tag{2}$$

where l is any arbitrary distance whose scale is set by l_0; however, since only differences in length are important here, no scale was set.

The following procedure indicates how the correction term to the value derived from linear interpolation may be obtained, provided that A and B are determined from the graph of $\Delta l/\Delta\lambda$ vs λ. Let

$$a = l' - l_1 = A(\lambda' - \lambda_1) + B(\lambda' + \lambda_1)(\lambda' - \lambda_1). \tag{3}$$

This may be written as

$$a = A(\Delta\lambda') + B(\lambda' + \lambda_1)(\Delta\lambda'), \tag{4}$$

where

$$\Delta\lambda' = (\lambda' - \lambda_1). \tag{5}$$

λ' is the wavelength to be determined by interpolation between the known wavelengths λ_1 and λ_2.

$$b = (l_2 - l_1) = A(\lambda_2 - \lambda_1) + B(\lambda_2 + \lambda_1)(\lambda_2 - \lambda_1) \tag{6}$$

or

$$b = A(\Delta\lambda) + B(\lambda_2 + \lambda_1)(\Delta\lambda), \tag{7}$$

where

$$\Delta\lambda = (\lambda_2 - \lambda_1). \tag{8}$$

Table I. Measurements on the $2\nu_1$ Band of $N_2{}^{14}O^{16}$ (Vac. cm^{-1})

J	$R(J)$	Calc.[a] − Obs.	J	$P(J)$	Calc.[a] − Obs.
0	2564.1809	+0.0089			
1	64.9964	0.0000			
2	65.8153	+0.0013	2	2561.6579	0.0000
3	66.6159	−0.0052	3	60.7986	−0.0077
4	67.4286	0.0000	4	59.9403	−0.0076
5	68.2327	+0.0070	5	59.0826	0.0000
6	69.0198	+0.0039	6	58.1878	−0.0228
7	69.7993	0.0000	7	57.3261	−0.0057
8	70.5709	−0.0050	8	56.4462	0.0000
9	71.3410	−0.0047	9	54.5472	−0.0067
10	72.1086	0.0000	10	54.6598	+0.0051
11	72.8480	−0.0165	11	53.7488	0.0000
12	73.6254	+0.0115	12	52.8324	−0.0038
13	74.3562	0.0000	13	51.9190	+0.0022
14	75.0821	−0.0097	14	50.9907	0.0000
15	75.8212	+0.0007	15	50.0605	+0.0026
16	76.5424	0.0000	16	49.1131	−0.0053
17	77.2494	−0.0080	17	48.1721	0.0000
18	77.9591	−0.0066	18	47.2283	+0.0091
19	78.6670	0.0000	19	46.2523	−0.0072
20	79.3636	+0.0020	20	45.2932	0.0000
21	80.0451	−0.0043	21	43.3239	+0.0036
22	80.7303	0.0000	22	43.3385	−0.0021
23	81.4083	+0.0039	23	42.3544	0.0000
24	82.0691	−0.0026	24	41.3590	−0.0025
25	82.7322	0.0000	25	40.3635	+0.0015
26	83.3798	−0.0069	26	39.3559	0.0000
27	84.0272	−0.0056	27	38.3481	+0.0049
28	84.6730	0.0000	28	37.3406	+0.0167
29	85.2965	−0.0098	29	36.2981	0.0000
30	85.9198	−0.0131	30	35.2695	+0.0042
31	86.5526	0.0000	31	34.2297	+0.0029
32	87.1698	+0.0041	32	33.1813	0.0000
33	87.7673	−0.0045	33	32.1311	+0.0017
34	88.3715	0.0000	34	31.0830	+0.0121
35	88.9637	−0.0006	35	30.0060	0.0000
36	89.5662	+0.0159	36	28.9435	+0.0092
37	90.1297	0.0000	37	27.8650	+0.0081
38	90.7074	+0.0051	38	26.7727	0.0000
39	91.2751	+0.0069	39	25.6871	+0.0051
40	91.8275	0.0000	40	24.5855	+0.0095
41	92.3763	−0.0028	41	23.4816	0.0000
42	92.9130	+0.0129	42	22.3602	−0.0117
43	93.4652	0.0000	43	21.2530	−0.0028
44	94.0140	+0.0062	44	20.1335	0.0000
45	94.5228	−0.0090	45	19.0129	+0.0081
46	95.0430	0.0000	46	17.8728	+0.0030
47	95.5467	−0.0090	47	16.7286	0.0000
48	96.0912	+0.0130	48	15.5786	−0.0026
49	96.5614	0.0000	49	14.4239	−0.0037
50	97.0470	−0.0073	50	13.2677	0.0000

[a] Values reported by Rank *et al.*[5]

a is the distance between λ_1 and λ', and b is the distance between λ_1 and λ_2. Let the value of λ' derived from linear interpolation be designated as λ'_{approx}:

$$\lambda'_{approx} = \lambda_1 + \frac{a}{b}\Delta\lambda = \lambda_1 + \frac{a}{A + B(\lambda_1 + \lambda_2)}. \tag{9}$$

Substituting for $b/\Delta\lambda$ from Eq. (7),

$$\lambda'_{exact} = \lambda_1 + \Delta\lambda' = \lambda_1 + \frac{a}{A + B(\lambda_1 + \lambda')}; \tag{10}$$

the value for $\Delta\lambda'$ used here was obtained from Eq. (4).

$$\begin{aligned}\lambda'_{approx} - \lambda'_{exact} &= a\left[\frac{1}{A + B(\lambda_1 + \lambda_2)} - \frac{1}{A + B(\lambda_1 + \lambda')}\right] \\ &= \frac{aB[(\lambda' - \lambda_1) + (\lambda_1 - \lambda_2)]}{[A + B(\lambda_1 + \lambda_2)][A + B(\lambda_1 + \lambda')]} \\ &= \frac{aB(\Delta\lambda' - \Delta\lambda)}{[A + B(\lambda_1 + \lambda_2)][A + B(\lambda_1 + \lambda')]} \\ &= \frac{-aB\Delta\lambda[1 - (\Delta\lambda'/\Delta\lambda)]}{[A + B(\lambda_1 + \lambda_2)][A + B(\lambda_1 + \lambda')]}.\end{aligned} \tag{11}$$

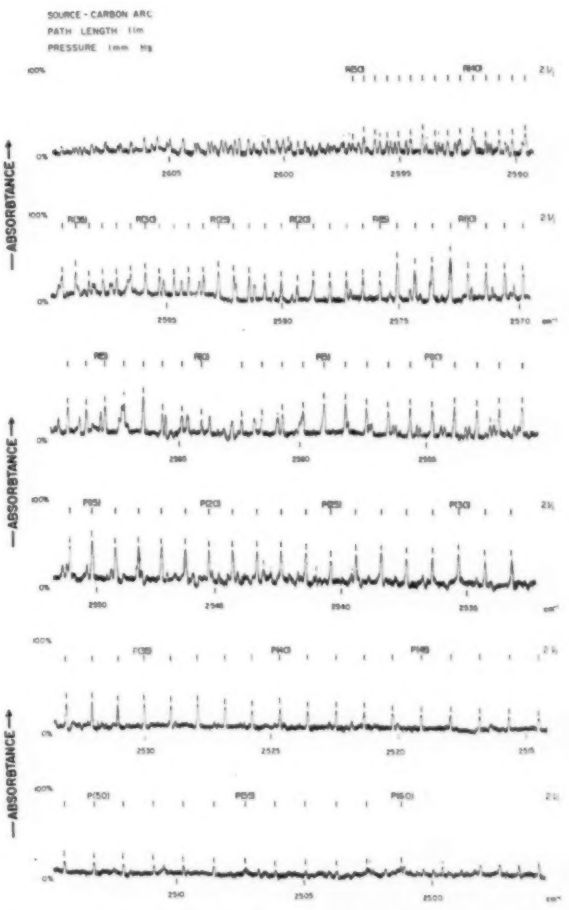

Fig. 2. N_2O bands in the region of 3.9 μ. The R and the P identifications refer to the $2\nu_1$ band of $N_2{}^{14}O^{16}$.

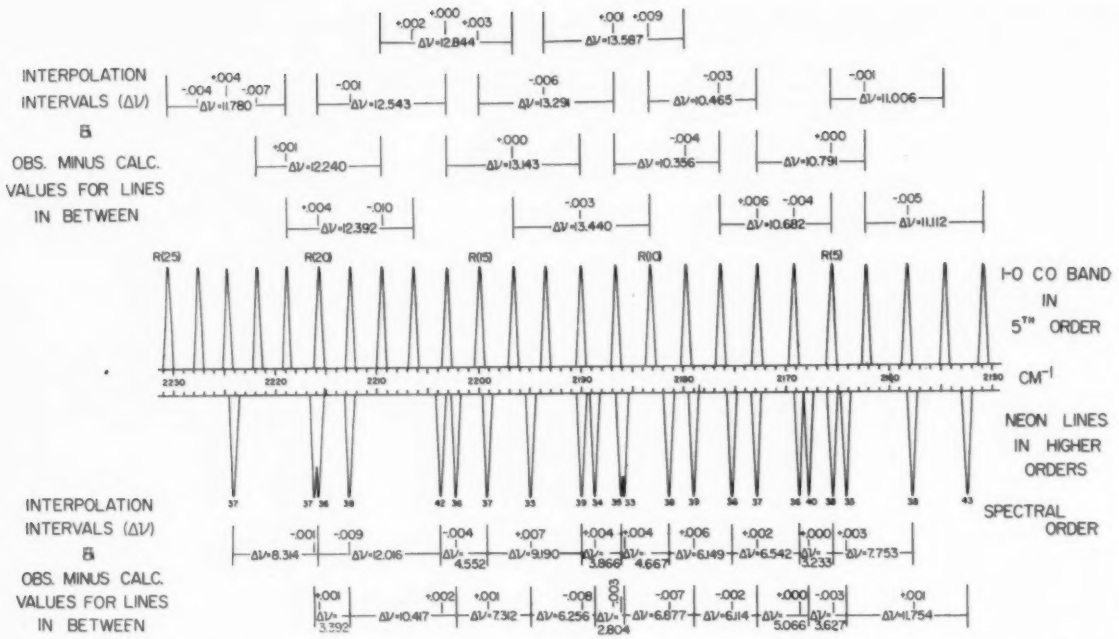

Fig. 3. Interpolations between the rotational lines of 1–0 CO band and between the higher-order neon lines observed in the same angular stretch of the grating.

If $(\lambda'_{approx} - \lambda'_{exact})$ is small, then

$$a/b \approx \Delta\lambda'/\Delta\lambda. \tag{12}$$

Using Eq. (12) in (11) gives

$$\lambda'_{approx} - \lambda'_{exact} = \frac{-aB\Delta\lambda[1 - (a/b)]}{[A + B(\lambda_1 + \lambda_2)][A + B(\lambda_1 + \lambda')]}. \tag{13}$$

Let us designate the right-hand side of Eq. (13) as the correction term. Then,

$$\lambda'_{exact} = \lambda'_{app.ox} - (\text{correction term}). \tag{14}$$

The correction term contains λ', which should be λ'_{exact}. At first, λ'_{approx} may be substituted for λ' and a value for the correction term may be evaluated. This leads to a λ'_{exact} by using Eq. (14). This value of λ'_{exact} may again be substituted in the denominator of the correction term to lead to a better λ'_{exact}. After a few iterations, one arrives at a good value for λ'_{exact}. Use of IBM computers facilitates these computations.

After determining spectral positions relative to calibration spectra, the absolute positions are obtained by applying the factor K mentioned earlier.

III. Results

The results obtained for the measurement of the rotational lines of the $2\nu_1$ band of the nitrous oxide molecule are given in Table I. The calculated values refer to the evaluations of Rank *et al.*[5] The lines identified by the underscore in the J value column have been used in determining the K factor. The positions of the remaining structure could be determined to an accuracy of ± 0.005 cm^{-1}. The $2\nu_1$ band of N_2O occurs in a region which is free from atmospheric absorptions, and it seems that its rotational lines can be conveniently used as secondary standards. It is important to note that the region of absorption of the $2\nu_1$ band is overlapped by other bands pertaining to the N_2O molecule. Therefore, one should exercise care in using only unblended lines as standards. To facilitate this, a pictorial reproduction of this band recorded with the present spectrograph has been shown in Fig. 2.

The validity of the integral relation between overlapping orders has been examined by making measurements on the fundamental vibration–rotation band of the CO molecule and the higher-order neon lines observed in the same angular stretch of the grating. It may be noticed from the data presented in Fig. 3 that linear interpolations can be made to a high precision in both the infrared CO band and the visible neon lines which incidentally have been observed in the 34th through 44th spectral orders. This problem has been elaborated before by Rao *et al.*[3] and Rank.[6]

The support of the Atomic Energy Commission through a contract made with The Ohio State University Research Foundation is gratefully acknowledged. The discussions with Darrell Burch during the designing of the grating drive proved useful.

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Of **Optics and Opticists** *continued from page 1100*

The two former Research Directorates, of Electronics and Geophysics, were abolished and their constituent laboratories, branches, and sections were regrouped along functional lines. The activities pertaining to astronomy and astrophysics, including radio astronomy, cosmic rays, and energy conversion, are all incorporated in the Space Physics Laboratory, as is the Sacramento Peak Observatory. The Space Physics Laboratory includes OSA members **J. W. Evans** and **L. S. Combes.** The activities pertaining to the ionosphere and physics and chemistry of the high atmosphere, including auroral physics, and the well-known groups performing spectroscopic research in the uv and xuv, are all incorporated in the Upper Atmospheric Laboratory. OSA member **Norman J. Oliver** has been named Senior Scientist of this Laboratory. Other OSA members in this Laboratory are **Y. Tanaka, H. E. Hinteregger, F. Leblanc, A. Jursa, O. Oldenberg,** and **H. Cohen.** The Laser group of **P. Schweitzer,** the High Temperature group of OSA member **Heinz Fischer,** and the thermal imaging group of **G. Ploetz** have been incorporated into the Optical Physics Laboratory, which continues to include the previous efforts in visibility, radiometry, luminescence, and infrared physics, and such OSA members as **J. S. Garing, R. G. Walker, B. Schurin, E. Loewenstein, G. Vanasse, A. T. Stair, R. Toolin, J. Grenier, J. Cahill,** and **J. N. Howard.** OSA member **C. E. Ryan** continues to be a Deputy Chief of the Solid State Sciences Laboratory and OSA Member **Shea Valley** continues in the Operations Division of the AFCRL staff. We were pleased to determine that this organization has more than 20 OSA members; how many organizations can top this?

Opticists on the move. . . .**Joseph Rood,** incoming president of the OSA Rochester Section, is also Program Chairman of the Glass Division of the American Ceramic Society's Meeting at Bedford Springs, Pa., in October 1963 and in Chicago in April 1964. . . .**Russell A. Temple,** formerly with Aerojet, has moved to Electro-Optical Systems as Manager of Optical Design and Fabrication. . . .**Richard C. Beitz** has been appointed Vice President-General Manager of Instruments Division of Barnes Engineering; he was formerly with Cornell Aeronautical Laboratory. . . .**J. Dyson** has been appointed the new superintendent of the Light Division of the UK's National Physical Laboratory (he was with AEI). . . .**John D. Harby,** with Bausch & Lomb since 1940, has been appointed general products manager for the Ophthalmic Division. . . .**Jurgen Meyer-Arendt,** one of our hard-working Patents Panelists, has moved from Utah State University to the National Bureau of Standards-Boulder. . . . **William B. Fussell,** past head of the Coatings Section at the Goddard Space Flight Center, has joined the Photometry and Colorimetry Section of the National Bureau of Standards, Washington. . . .**Klaus D. Mielenz** has joined the Metrology Division of the NBS. . . .**P. Jacquinot** has been appointed head of the CNRS-France. . . .**W. E. K. Middleton** has retired from the National Research Council (Canada); a former director of OSA and Ives Medalist in 1959, Dr. Middleton has interested himself in the historical rather than the developmental aspects of science lately. His translation of Bourget's *The Graduation of Light* was published in 1961, and he is presently finishing a history of the barometer. . . .**John R. Yoder** will direct laser applications research at Barnes Engineering.

Awards made. . . .The Thomas Young Medal of 1P²S* to **Charles H. Townes** *MIT* and **Arthur L. Schawlow** *Stanford U.* for their early work on the laser. . . .to **David L. MacAdam,** Senior Research Associate in the Physics Division and head of the Image Structure Department of the *Eastman Kodak Research Laboratories,* and OSA's immediate past-president, the Godlove Award for his outstanding contributions to the knowledge of color in science, art, and industry. . . .to **William F. Meggers** *NBS* the 1963 Award of the Spectroscopy Society of Pittsburgh. . . .to **Richard Tousey** *NRL* the Henry Draper Award of the National Academy of Sciences for his original investigations in astronomical physics. . . .to **Norman J. Oliver** *AFCRL* the "award" of having the geographical feature located at 84° 56′S latitude, 173° 45′W longitude, east of Shackleton Glacier at the head of Ross Ice Shelf, Antartica, named Mount Oliver. . . .to **Joseph C. Richmond,** *NBS* ceramic engineer, the U.S. Dept. of Commerce Silver Medal for Meritorious Service, citing his outstanding contributions to the accuracy and standardization of thermal radiation measurements so necessary to the space program. . . .to **Charles H. Corliss** the U.S. Dept. of Commerce Silver Medal for Meritorious Service. Mr. Corliss, a physicist in the NBS Spectroscopy Section, has made outstanding contributions to the fields of quantitative spectroscopy, especially the determination of absolute transition probabilities. . . .and to **Manfred H. Rees,** research associate in the U. of Colorado's Laboratory for Atmospheric and Space Physics, a $130,000 NSF grant to continue, with his colleague **William A. Rense,** their studies of aurora borealis and other upper atmospheric phenomena begun some six years ago.

Maser minutiae. . . .Compact, self-contained optical calorimeters for measuring the output energy and power of pulsed and cw masers and now marketed by four companies, **Optics Technology, Laser Systems Center of Lear Siegler, Westinghouse,** and **TRG** . . . . The **Korad Corporation's** president, T. H. Maiman, announced in March the achievement of a ruby maser pulse with a peak power of 500 MW. The pulse width was approximately 7 nsec . . . . **NBS** scientists have obtained interference fringes—formerly visible over an optical path of less than 2 m—over a 200-m path. A maser was used as the light source to produce this phenomenon. Work is now underway to stabilize the maser equipment so that interferometric calibrations of length-measuring devices may be made with this maser . . . . **Stanford Medical Center,** in conjunction with **Optics Technology, Inc.** and **NIH,** are developing a maser to correct serious eye conditions . . . . The **Raytheon** house organ *Electronic Progress,* Vol. VII, January-February 1963 (No. 4), is devoted to a state-of-the-art report on masers.

Readers' attention is drawn to . . . . "A Far Infrared Bibliography" by **E. D. Palik,** which appeared in abbreviated form in

* Great Britain's Institute of Physics and Physical Society.

J. Opt. Soc. Am. **50,** 1329 (1960), has now appeared in an expanded, cross-indexed form as NRL Bibliography No. 21 and is available from Office of Technical Services, Dept. of Commerce, Washington 25, D.C., for $1.50 . . . . a classified (Secret) Journal of Missile Defense Research will commence publication in October 1963, under the editorship of **S. S. Penner** *IDA*, for ARPA. The purpose of creating this journal is to provide prompt publication of important research contributions which cannot be printed in the open literature for reasons of national security . . . . *Coordinated Color Identification for Industry*, by **Kenneth L. Kelly** *NBS*, describes a method of coordinating the five levels of fineness of color designation which was developed by the Inter-Society Color Council Subcommittee for Problem 23, The Expression of Historical Color Usage. Available from the Supt. of Documents, U.S. Government Printing Office, Washington 25, D.C., $0.15 . . . . *Bibliography on Analytical Flame Spectroscopy*, by **R. Mavrodineanu,** is now available *with punchcard index* (a supplement to the Bibliographies originated by **M. Margoshes** *NBS*). Both volumes $15.00 each may be ordered from P.O. Box 7164, Baltimore 18, Md. . . . . and to *The Organization of Scientific Research in the United States*, prepared by Mary E. Corning of the NSF Office of International Science Activities, the first time US academic, industrial and private scientific activities have been compiled into a single document.

News from **Russia** this month includes the publication of an annotated bibliography of USSR Literature on *X-ray and Optical Spectra* by the Aerospace Information Division of the Library of Congress . . . . and the following extract from the Decisions of the 1962 November Plenum of the Central Committee of the Communist Party of the Soviet Union, published in *Optika i Spektroskopiya* "Soviet workers in **optics and spectroscopy,** like the representatives of other sciences, are confronted with the task of strengthening the creative growth of new branches of their disciplines and of improving their links with related sciences. The theoretical and experimental study of the processes of emission and absorption of light by a substance opens previously unseen scientific and technical vistas. Optical methods are uniquely valuable for solid-state physics, the physics of large molecules and polymers, and so on. Close contact of experts in optics and of spectroscopists with chemists is very important. As before, the development and introduction into production of new methods of spectral analysis, especially of molecular spectral analysis, is an important practical problem. It is also necessary to work actively and persistently on the creation of more highly perfected optical and spectral apparatus and to work out optical methods for the automation of production processes. The use of new principles of observation and measurement, and of the transfer, recording, and treatment of information, makes it possible to penetrate deeper and deeper into physical regularities and to accelerate the tempo of scientific investigations. We need to introduce the achievements of optics and spectroscopy skillfully and swiftly into the public economy. A great army of scientists, builders, engineers, and inventors connected with production is working in the Soviet Union. The tasks set by the November Plenum are inspiring them to new accomplishments, the purpose of which is to speed the creation of the material and technological basis of Communism." Some readers do not like our publishing foreign papers or such information as the foregoing. We feel it important, not only for the furtherance of science but for the furtherance of international relations and their betterment, to know as much about our foreign colleagues and the climate in which they think, move, and have their being as we possibly can—and, of course, for them to know as much about us. It may come as a shock to some readers to realize that some 20% of our subscribers are foreign. The Nobel Prize-winning physicist, Dr. Tamm, made the point in a CBS program in May that everybody distrusted everybody else. A way to overcome distrust (which is fear) is to learn about the other fellow, and to communicate with him.

National Bureau of Standards news from Boulder and Washington, D.C. . . . NBS has developed equipment and procedures for **growing large, single crystals from aqueous solution.** The crystals are used in studies of crystal growth phenomena and as reference materials in measurements of the chemical and physical properties of the solid state. This may be read in J. Research NBS **67C**, 25 (Eng. & Inst.)(Jan.–Feb. 1963) . . . . The 9 July 1962 high-altitude nuclear explosion created a man-made belt of high-energy electrons. NBS, in cooperation with the Geophysical Institute of Peru, has made a **series of measurements of the synchroton radiation** emitted by these electrons. Calculations based upon these measurements have provided an estimate of the number, energy spectrum, and decay rate of the electrons. More information about this will be found in the J. Geophysical Res. and also in an article in Science **138,** 5 (5 Oct. 1962) . . . . In recent experiments at NBS, mercury and potassium crystal whiskers were grown from the vapor phase in an electron field emission tube. It was possible, it appeared, **to determine the growth kinetics of the crystals** thus produced from the patterns that appeared on the fluorescent screen of the tube. Results of the mercury experiments were in good agreement with those of other investigators. The potassium experiments were the first known use of an alkali metal as a field emitter, and showed several new effects. For further technical details, see J. Chem. Phys. **27,** 1606 (1962) . . . . A technique for **measurement of vibration displacement-amplitudes** increases the precision of calibration methods for vibration pickups. This technique used a Fizeau-type interferometer with a monochromatic light source and a photomultiplier tube to sense changes in the interference pattern. Vibration amplitudes are identified in the presence of jitter with greater sensitivity than by previous visual means. Read more about this in J. Acoust. Soc. Am. **34,** 455 (1962) . . . . A simplified method for **sealing sapphire windows to glass tubes** has been devised at NBS. Graded seals made by this technique are vacuum-tight and are capable of withstanding temperatures as high as 400°C and as low as −195°C. For further information on this method, readers should contact the NBS Office of Technical Information . . . . NBS is tentatively planning a series of **Precision Measurement Seminars,** as one way of meeting its responsibility to disseminate information concerning standards, calibration, and measurement techniques to science and industry. These seminars, planned to last from a few days to no more than two weeks (depending on the subject) will be held at both Washington and Boulder. No charge will be made for attendance at the seminars. If sufficient interest is shown, seminars will be offered in: acoustical measurements (W); attenuation measurements at communications frequencies (B); frequency comparison techniques (radio frequencies and atomic standards) (B); precision and accuracy in measurement and calibration (W); and length measurements (W). Laboratories interested in having their personnel attend any of these seminars should write for the (W) seminars to W. R. Tilley, Office of Technical Information, Rm. 500, South Bldg., NBS, Washington 25, D.C., and for the (B) seminars to E. H. Brown, Education Director, NBS, Boulder, Colorado.

The new **Boettcher Center for Science, Engineering and Research** at the U. of Denver was formally dedicated in February this year, and two OSA members were among the featured speakers: **W. R. Brode,** former editor of J. Opt. Soc. Am., and national past president of Sigma Xi, addressed the Engineers' Day Convocation; **David Gates,** Consultant to the Director, Physics of the Atmosphere, NBS-Boulder, and *Applied Optics* Denver Reporter, participated in a seminar on "The Challenge of a Partnership between Technology and the Life Sciences". The Boettcher

continued on page 1173

Quantitative Infrared Spectroradiometry of Liquid Propellant Flames

Richard H. Tourin

Quantitative infrared spectra of hot gases are of use in schemes to predict radiances of large flames. An infrared spectroradiometer equipped for digital readout of spectra has been used to measure infrared spectral absorptances and radiances of flames burning a variety of nitrogenous and carbonaceous liquid propellants. Representative flame spectra are presented for several propellant types. The results illustrate that flame spectral radiances depend primarily on temperature, pressure, and composition; fuel characteristics play a part mainly in determining the values of the primary variables. There are some interesting connections between this work and the early researches of Coblentz and his contemporaries.

I. Introduction

The infrared radiation of flames has been a subject of investigation for many years. Beginning around 1890, many measurements have been reported of infrared spectra of various flames. The earliest workers were concerned with establishing the laws of thermal radiation, in particular with checking experimentally the theoretical formulae of Kirchhoff, Planck, and Wien, as they apply to flames, and in identifying the chemical species contributing to flame radiation.[1-12] Later, infrared spectra of flames were measured in connection with studies of molecular structure and combustion processes.[13-17] More recently, absolute infrared spectral radiances of flames have been extensively measured to meet the needs of military and space applications. These recent measurements cover infrared spectra of gas flames,[18] liquid propellant flames,[19-21] solid propellant flames,[22] gases heated in gas cells in a furnace,[23-30] rocket flames,[31-33] and shock-heated gases.[34] Infrared absorptances of gases heated by these different methods have been compared and correlated with theory.[30,35] In this work, the infrared spectral band emission of hot gases was found to be determined by temperature, pressure, and gas composition, independent of the method of heating.

An important purpose of recent infrared flame measurements has been to provide input data to schemes for predicting the infrared spectral radiances of large flames, under various conditions. The methods of prediction are chiefly based on the so-called band model approach,[36] in which one tries to substitute a tractable mathematical representation in place of an actual infrared band spectrum consisting of many hundreds or thousands of spectral lines. Flame radiance predictions have been made successfully in a number of cases, although the extent of current work on empirical infrared flame measurements demonstrates that no prediction method has achieved wide acceptance in application.

Flame radiation studies in this laboratory have been concerned particularly with the dependence on fuel and oxidizer characteristics of infrared radiances of flames burning rocket propellants. Although the molecules produced by combustion of the newer propellants are mostly very familiar—in particular, carbon dioxide and water vapor, whose spectra are well-known—the absolute spectral radiances observed in flame radiation vary with flame parameters and vary from one propellant combination to another, and present theory cannot predict these radiances reliably from first principles. But when the spectral measurements are obtained for known values of flame parameters, they are useful for predicting flame radiances for other values of these parameters, by means of the prediction methods already mentioned. Such measurements, for flames burning liquid propellants, form the principal subject of this paper.

II. Historical Note

It is appropriate to recall the work of Coblentz and his contemporaries on infrared flame spectra, although a complete historical review is beyond the scope

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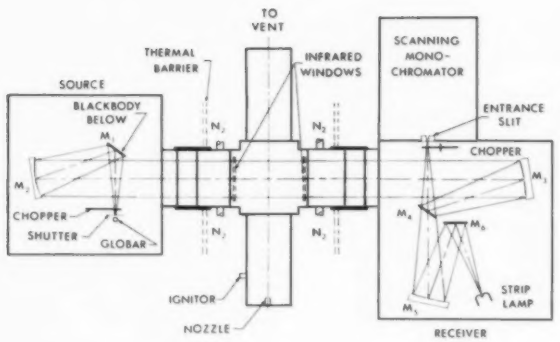

Fig. 1. Experimental setup for measurement of flame spectral radiance and absorptance. Fuel and oxidizer are sprayed from the section marked "nozzle", and the flame burns between this point and the downstream end of the tube. The spectroradiometer is essentially a single-beam, single-pass spectrometer, arranged to measure emission spectra, absorption spectra, and calibration spectra in rapid succession. The optical path is flushed with dry nitrogen to minimize the effects of atmospheric water vapor and carbon dioxide.

of this paper. The main features of the infrared spectra of hydrocarbon–air flames were known to Coblentz in 1905,[1] largely from the classic experiments of Paschen.[2–4] Comparing atmospheric absorption measurements to the emission measurements of Paschen[2] and of Rubens and Aschkinass,[5] Coblentz observed that a rise in temperature shifts the 4.26-μ CO_2 band to 4.40 μ. Coblentz suggested[6] that this shift might be due to dissociation into CO and a consequent shift toward the absorption band of CO "at 4.59 μ". This idea seemed to be confirmed when he found a band with a peak at 4.65 μ in the emission spectrum of the graphite arc.[7] However, he noted that his explanation of the CO_2 band shift was inconsistent with atmospheric absorption measurements of Langley, which showed a broad band from 4.30 to 4.65 μ, since CO is not found in significant quantity in the atmosphere. He concluded that the mechanism producing the CO_2 radiation was not understood and further experiments were needed.

The CO_2 band shift was explained many years later with the aid of quantum theory. It is due in part to contributions from excited vibrational levels of the CO_2 molecule, which are not appreciably populous at room temperature,[16,24,26] and in part to population of higher rotational energy states within each vibrational state.[27]

In his study of the infrared emission spectra of the Bunsen, acetylene, and amyl acetate flames, Coblentz pondered the significance of the term "temperature" as applied to a flame,[8] anticipating current concern with this problem. He tried to determine flame temperature from the position of the spectral maximum in several different flame bands. This naturally gave inconsistent and confusing results, because the Wien displacement law does not apply to band spectra.

Coblentz also investigated the flame of carbon disulfide burning in air,[9] and he measured infrared emission spectra of gases in a vacuum tube.[10] He speculated about the possible nonthermal nature of this latter radiation, which he referred to as "luminescence".

In view of current work, it is interesting to note that the possible effect of the method of heating on the infrared spectra of hot gases was a subject of discussion in the early days of this century. Fredenhagen[11] suggested that the observed band spectra of flames might be due to the chemistry of the combustion process rather than to the heating of the gas, and Fredenhagen believed a gas heated in the absence of combustion would give a continuous spectrum instead of a band spectrum. In order to investigate this question, Schmidt,[12] in 1913, measured the infrared spectrum of pure carbon dioxide in a quartz gas cell heated in an electric furnace and verified that a hot gas does indeed emit infrared band spectra regardless of the method of heating.

III. Experimental

A. Methods and Apparatus

Spectral radiances of solid materials are commonly determined by comparing the sample radiance to radiance of a blackbody. For gases, it is often more accurate and elucidating to measure spectral absorptance and spectral radiance at a few wavelengths, from which gas temperature can be determined,[16,38] and then to calculate spectral radiance at other wavelengths from absorption measurements, using the Kirchhoff relation,

$$N_\lambda(T) = \alpha_\lambda(T) N_\lambda^b(T), \tag{1}$$

where $\alpha_\lambda(T)$ is spectral absorptance at wavelength λ, and $N_\lambda^b(T)$ is the value at the same wavelength of the Planck radiance function at the measured temperature T. In this procedure, the tedious and exacting process of comparison to a blackbody source is obviated. A blackbody source is needed only once: to establish a calibration point for the temperature measurement.[38] If absorptance is very small ($\lesssim 5\%$), the accuracy of this method is reduced, and the direct radiance comparison must be used. The absorptances of most of the flames studied in the present work were sufficiently high to apply Eq. (1) with satisfactory accuracy.

The combustion system and the infrared spectroradiometer used in this work, and the data reduction procedures, are quite complex, because of the many stringent requirements that must be satisfied to obtain absolute flame spectra free from serious error. Among the essential requirements are elimination of atmospheric absorption effects, accounting for self-absorption and temperature gradients in the flame, correction for effects of windows, and avoidance of vignetting in the optical system. In addition, the flame must burn at constant pressure, temperature, and composition

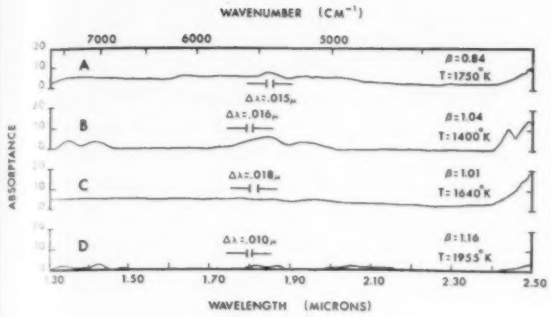

Fig. 2. Infrared absorptance of four flames in the spectral region 1.30–2.50 μ. Optical path is 12.7 cm. Equivalence ratios and corresponding temperatures and spectral slit-widths are given on the figure for each curve. The temperatures are averages over the flame path determined from the infrared measurements, described in the text. The four curves are as follows:

Curve A: kerosene–oxygen, equilibrium composition CO_2 35.7%, H_2O 45.0%, CO 14.3%, H_2O 0.5%.

Curve B: ammonia–oxygen, composition H_2O 74.0%, N_2 24.6%, O_2 1.4%.

Curve C: hydrazine (N_2H_4)–oxygen, composition H_2O 66.4%, N_2 33.2%, O_2 0.4%.

Curve D: JP4 (a mixture of hydrocarbons)–nitrogen tetroxide (N_2O_4), composition CO_2 31.3%, H_2O 33.0%, O_2 7.6%, N_2 27.8%, OH 0.1%, NO 0.2%.

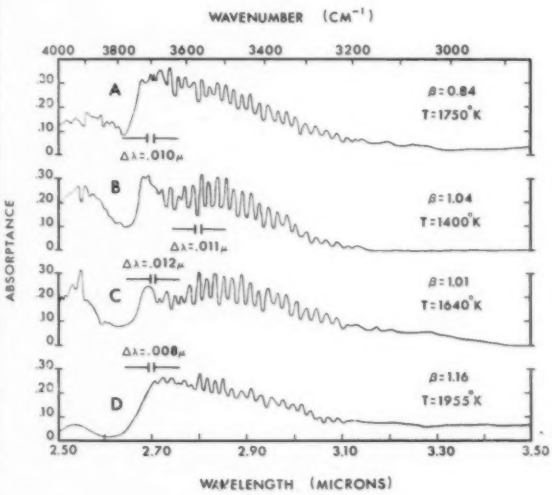

Fig. 3. Infrared absorptances of four flames in the spectral region 2.50–3.50 μ. Curves A, B, C, and D, respectively, are continuations of the curves of the same designation shown in Fig. 2.

over the time needed to make the measurements. Satisfying these requirements for a broad range of propellants, at various mixture ratios, is no mean task. Detailed descriptions of the apparatus are given in technical reports.[19–21]

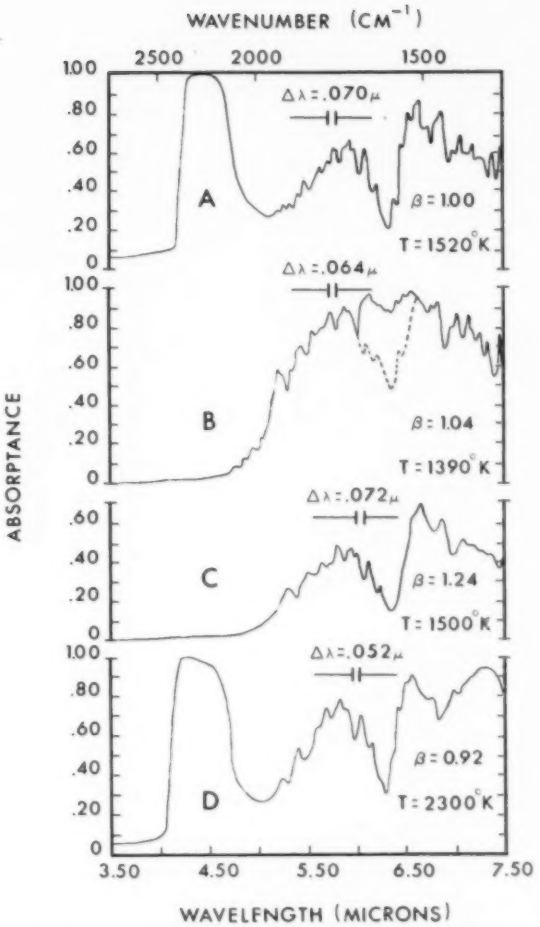

Fig. 4. Infrared absorptances of four flames in the 3.50–7.50 μ region. The fuel combinations and oxidizers used are the same as for Figs. 2 and 3, except that curve A is for hexane–oxygen instead of kerosene–oxygen. The prominent peak near 4.50 μ in curves A and D is mainly due to carbon dioxide; the remainder of the spectral features correspond to water vapor bands. Curve B shows an example of the effects of flushing the optical path with dry nitrogen. The solid curve shows measurements made without flushing the optical path thoroughly during the measurement. The dashed curve shows the change in the spectrum when the optical path was flushed. The difference is due to the absorption by cold water vapor in the products of combustion. The relevant chemical data are as follows:

Curve A: hexane–oxygen, composition CO_2, 46.1%, H_2O 53.9%.

Curve B: ammonia–oxygen, composition H_2O 74.2%, N_2 24.7%, O_2 1.1%.

Curve C: hydrazine–oxygen, composition H_2O 61.7%, O_2 7.5%, N_2 30.8%.

Curve D: JP4–N_2O_4, composition CO_2 29.9%, H_2O 25.9%, CO 6.4%, N_2 25.5%, H_2 2.3%.

Figure 1 shows the optical arrangement of the burner system and spectroradiometer. This setup enables measurement of absorption and emission spectra of a flame, and calibration, in rapid succession, for a wide variety of liquid propellant combinations. The only

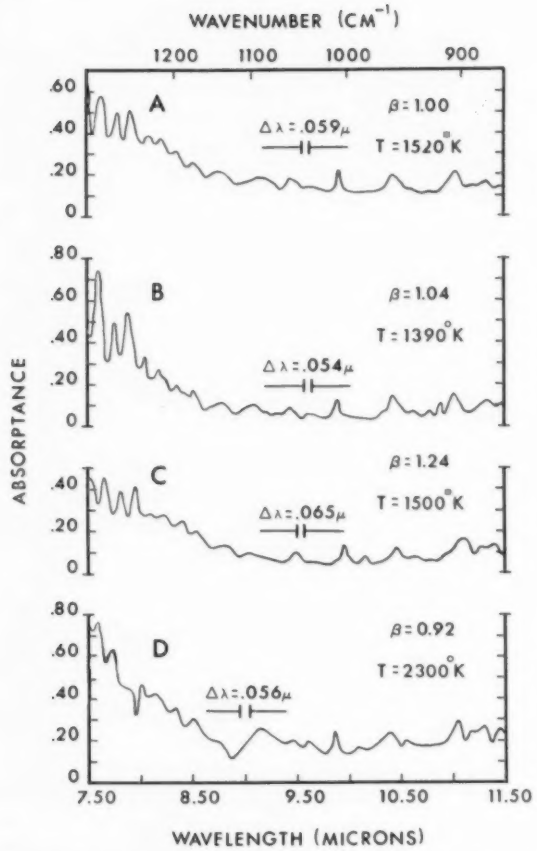

Fig. 5. Continuations of the curves shown in Fig. 4, in the region 7.50–11.50 μ. The spectral structure is due to water vapor and is very similar for all four flames.

really novel feature of the spectroradiometer is the use of a digital readout detection system to obtain the spectral data on punched paper tape.[21] This was found necessary because of the large volume of data to be handled. Data gathering and processing were completely automated with the aid of this system. The spectroradiometer provides the flame emission and absorption data on paper tapes. These are converted to magnetic tape for processing. Auxiliary data (for example, wavelength calibration and window transmittance) are stored permanently on a reference magnetic tape. The measurement tape and reference tape are fed simultaneously to an IBM 7074 computer. The magnetic tape output of the 7074 is converted to plots of spectral absorptance vs wavelength, radiance vs wavelength, and temperature, by an Electronic Associates data plotter.

B. Results

Some representative examples of liquid propellant flame absorption spectra are given in Figs. 2–6. A large number of spectra of this type has been measured for many propellant combinations.[19–21] Figures 2 to 6 show plots of spectral absorptance vs wavelength for four flames—hydrocarbon–oxygen, ammonia–oxygen, hydrazine–oxygen, and JP4–nitrogen tetroxide—of known temperature, pressure, and composition. The spectral radiance at any wavelength can be computed by multiplying the measured absorptance by the proper value of the Planck function for that wavelength. The different spectral regions were measured under slightly different conditions, accounting for the variations in temperature. In Figs. 2 to 6, mixture ratio (oxidizer mass flow/fuel mass flow) is given in terms of equivalence ratio β, defined as the ratio of the mixture ratio itself to the stoichiometric mixture ratio. The equilibrium composition of each flame was calculated by the method of Damkohler and Edse, as described by Gaydon and Wolfhard,[39] using equilibrium constants given by Lewis and von Elbe.[40]

No explicit corrections were made for the effect of spectrometer slit function. The slit-function error is not very significant as long as the absorptances present

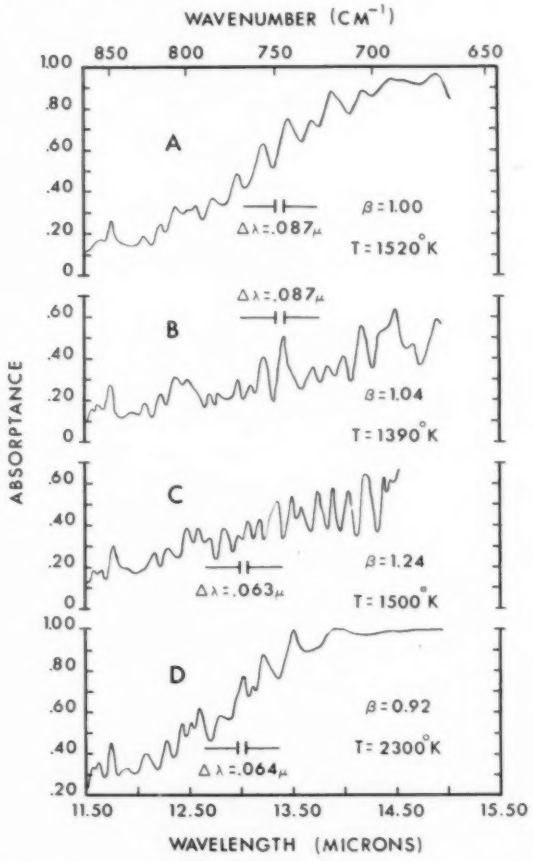

Fig. 6. Continuations of the curves of Figs. 4 and 5 in the region 11.50–15.50 μ. The structure in curves B and C is entirely due to water vapor, while curves A and D show contributions from the 15-μ bands of CO_2, superimposed on the water vapor spectrum.

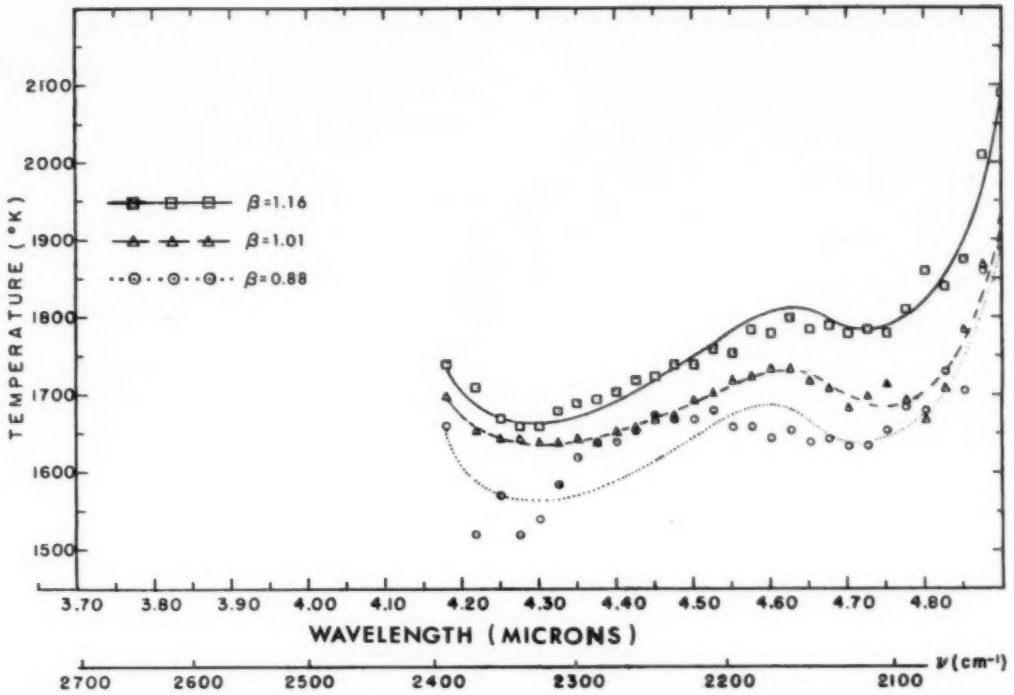

Fig. 7. Typical temperature vs wavelength plots, obtained by computing the ratio of spectral radiance to spectral absorptance from the measured spectral data independently for each wavelength. The variation of temperature with wavelength reflects the variation in temperature along the flame optical path, as discussed in the text.

are understood to be averages over a spectral bandwidth encompassing many rotational lines.[41] The accumulated errors of measurement yield an estimated uncertainty of ±0.03 for the values of absorptance plotted in Figs. 2 to 6. The uncertainties in temperature are in the range 75–125°K, including the effects of temperature gradients as well as measurement errors.

Flame temperatures were determined from the spectral radiance and absorptance measurements.[38] At any wavelength, the ratio of radiance to absorptance equals the value of the Planck radiance function at that wavelength, as shown in Eq. (1). A set of radiance to absorptance ratios for various wavelengths gives us a means of calculating the gas temperature from many independent experimental data. When we do this for a flame, we obtain curves of the type shown in Fig. 7. Different temperature values result from measurements made at different wavelengths. Generally, the calculated temperature is relatively higher at wavelengths where the absorptance is relatively lower. This apparent variation of temperature with wavelength has been a subject of considerable investigation.[16,42,43] It is caused by self-absorption in the presence of nonuniformity of flame temperature. Flames are characterized by large temperature gradients, and the variation of temperature with wavelength reflects the temperature variation along the optical path through the flame. The temperatures indicated for the curves in Figs. 2 to 6 are average flame temperatures determined in each case from a plot like Fig. 7, based on spectral measurements in either the 4.3-μ CO_2 bands or the 2.7-μ H_2O bands.

1. Hydrocarbon–oxygen flames: In Figs. 2 to 6, the curves marked "A" are absorption spectra of hydrocarbon–oxygen flames. Hexane and kerosene were used for fuel. The spectra are made up of many overlapping bands of CO_2 and H_2O. The spectra were found to vary very little with fuel composition or mixture ratio.

2. Ammonia–oxygen flames: Curves "B" in Figs. 2 to 6 are ammonia–oxygen flame absorption spectra. They appear to consist entirely of water bands. Attempts were made to determine the presence of unburned ammonia or various other species, such as NO and NH. No spectra of such species could be identified. This may have been due in part to overlapping of weak NO or NH bands by the strong H_2O bands.

The observed ammonia–oxygen flame temperatures are lower than those for hydrocarbon–oxygen flames, because the ammonia–oxygen flames have lower adiabatic combustion temperatures than do hydrocarbon–oxygen flames.

The spectral structure from 4.9 μ to 15 μ is due to the 6-μ water bands. There is no indication in this region of the presence of other species.

3. Hydrazine–oxygen flames: Curves "C" in Figs.

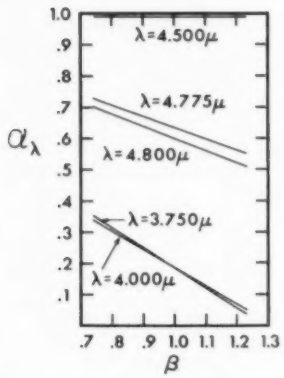

Fig. 8. The effect of mixture ratio on the continuous absorption in the spectrum of a flame burning JP4 with N_2O_4.

2 to 6 are the spectra of hydrazine–oxygen flames. Like the spectra of the ammonia–oxygen flames, they consist entirely of water bands. The range of flame temperature is 1500°K to 1900°K, higher than for the ammonia–oxygen flames.

4. JP4 with nitrogen tetroxide: The molecular bands of CO_2 and H_2O characterize the spectra of JP4–N_2O_4 flames, shown by the curves marked "D" in Figs. 2 to 6. Strong continuous absorption was measured over the entire wavelength region for rich mixtures, due to carbon formation.

The variation of continuum absorptance as a function of mixture ratio was measured at several wavelengths, as shown in Fig. 8. Changing the mixture ratio from lean (β = 1.23) to rich (β = 0.74) caused the absorptance to increase from 6% to 35% at 3.75 μ and 4.00 μ, where there are no molecular bands, and from 54% to 74% at 4.775 μ and 4.800 μ, where hot CO_2 is strongly absorbing; there was no effect at 4.500 μ, where the CO_2 band absorptance alone is nearly 100%.

IV. Discussion

The results presented in this paper illustrate the well-known facts that infrared spectra of flames are composites of the spectra of the molecules comprising the flame and that the spectral radiances depend primarily on temperature, pressure, and composition. However, flame spectral radiances in the infrared are not completely independent of fuel characteristics, because the temperature and composition of the flame gases are partly determined by fuel chemistry. Appreciable differences among spectral radiances of various flames are apparent in Figs. 2–8.

Table I illustrates that spectral absorptances determined from spectra of flames burning different fuels, as well as from spectra of heated pure gases, are equal for corresponding temperatures and quantities of radiating species. Data for CO_2 and H_2O heated in a gas cell are given in Table I, for comparison to the flame data. Although the available data are insufficient for a precise comparison, it is apparent from Table I that, for a given optical depth of an infrared-active molecule and given total pressure and temperature, the observed absorptance is independent of the chemical origin of the molecule. Here, we are following directly in the footsteps of Schmidt,[12] who first showed that hot gases obey Kirchhoff's law of radiation. The only thing we have added is to make the spectral measurements on an absolute quantitative basis.

The predominantly thermal excitation of infrared flame spectra is in marked contrast to the case of ultraviolet flame spectra, which are very sensitive to flame chemistry, and for which the excitation is often of chemical rather than thermal origin. The contrast in this respect between infrared and ultraviolet flame spectra has been discussed by Benedict and Plyler.[44] The essential difference is the internal degree of freedom giving rise to the radiation. Infrared band spectra are

Table I. Infrared Spectral Emittances and Absorptances of Flames[a]

λ (μ)	Fuel	Optical depth CO_2 (cm-atm)	Optical depth H_2O (cm-atm)	T (°K)	α_λ	$W_\lambda \times 10^{-4}$ (W cm^{-2} cm$_{\Delta\lambda}^{-1}$)
2.70	Hexane–O_2	4.3	6.2	1650–2000	0.32	4.4
2.70	Kerosene–O_2	4.5	5.7	1670–2100	0.33	4.7
2.70	Methanol–O_2	4.2	8.4	1525–1900	0.41	4.3
2.70	Gas cell[b]	—	4.18	1273	0.28	1.1
2.70	Gas cell[b]	—	7.26	1273	0.34	1.3
4.40	Hexane–O_2	4.3	6.2	1650–2000	0.97	3.5
4.40	Kerosene–O_2	4.5	5.7	1670–2100	0.97	3.7
4.40	Methanol–O_2	4.2	8.4	1525–1900	0.98	3.0
4.40	Gas cell[b]	4.3	—	1273	0.95	1.7
4.40	Gas cell[b]	4.5	—	1273	0.95	1.7
4.40	Gas cell[b]	4.2	—	1273	0.94	1.7
2.70	Hydrazine–O_2	—	8.4	1550–1730	0.30	3.2

[a] The measured spectral absorptances α_λ were multiplied by the value of the Planck spectral emittance function $W_\lambda^b(T)$ for the mean flame temperature to obtain the values of W_λ given in the table. P = 1 Atm.

[b] Total pressure 700 mm Hg, nitrogen added.

due to vibrations and rotations of molecules, involving motions of the atomic nuclei which make up the basic molecular framework, while ultraviolet band spectra result from the motions of the electrons in bound molecular states. In the former case, the radiative lifetime associated with the radiation is much greater than the mean time between gas kinetic collisions, while in the latter it is of the same order. Hence, molecules are much more likely to be in thermal equilibrium within their vibrational and rotational energy modes than they are with respect to excited electronic states.

The author is grateful to G. J. Penzias for assistance in checking the data, and to H. J. Babrov and G. A. Hornbeck for helpful discussions and criticisms.

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Books *continued from page 1108*

Color in Business, Science, and Industry has in the past been the outstanding reference work of color scientists, including those in business and industry. With the additional material introduced in the new edition, this will be more true than ever. It is really a treatise on Color . . . Science, rather than one on Color in Business . . . and Industry, and it provides the reader with a large part of the scientific information and with many of the ideas which will provide the stimulation for further development of the science of colorimetry.

HENRY HEMMENDINGER

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From the Editor

We have been asked to devote an editorial to referees and refereeing. Most of you on the receiving end of this journal have probably not functioned as referees, and your only opinion on the matter seems to be that if the standards of our referees were higher there would be fewer duds among these pages. Your Editor, however, is in daily contact with three classes of people from our journal audience: authors, whose chief characteristic is impatience; referees, whose chief characteristic is indignation; and critics, whose chief characteristic is omniscience.

How does one qualify to be a referee? About a year before this journal appeared we circulated to every member of the Optical Society of America a postcard asking each, among other things, what did he consider his area of speciality. From several hundred responses we selected, after much discussion, our initial pool of referees. This list has continued to grow and now includes several names in each of over 150 categories of specialty. There are those of you who seem to feel that our referees constitute some sort of secret society from which you are excluded. This is not so: convince us that you are ready willing, and able to read papers in the field of phase microscopy and we will send you a paper on phase microscopy by return mail. Each of our manuscripts is read by at least two readers, and when two specialists in the field of a manuscript are in agreement on "accept without change" or "reject", your Editor does not spend much time looking either for flaws or for saving graces. These situations occur, however, only about twenty percent of the time; in eight out of ten papers the advice from the readers is "accept after revision or condensation". Here the referee attempts to maintain the standards of the journal and at the same time attempts to help the author improve his paper by pointing out sections that are poorly written, nomenclature that is confused or ambiguous, pertinent references that appear to have been omitted, or just plain mistakes. He—the referee—also helps by advising the Editor whether this material is actually of general interest. With two sets of comments such as these, which can be submitted anonymously to the author, the task of the Editor is fairly straightforward. He scans the paper for additional editorial changes, chiefly in terminology, format, and units; and then sends a copy of the manuscript back to the author with a request that he consider these suggestions.

When the revised manuscript is returned to the Editor he reads it again, page by page alongside the original copy which he had retained, and compares the changes with the recommendations of the readers. One or two authors have somewhat surprised the Editor by writing, "Here is my revised manuscript. I have incorporated the changes suggested by the readers", and enclosing a manuscript identical with the original. A few return the original manuscript along with a long letter explaining to the editor that each of the points alleged as shortcomings by the readers becomes obvious if one differentiates all the equations, changes limits and variables, and then re-integrates. However, most authors cheerfully give in (or at least pretend to) and make some if not all of the requested changes.

In the puzzling cases, where the author appears to be recalcitrant, or where the two readers themselves had disagreed, one recommending acceptance and the other rejection, it has been our practice to turn to an "umpire", chosen from those of our associates on whose wisdom, experience, and detachment we have come to rely. We send him the entire package of manuscript and readers' comments (here not anonymous) and ask him for a considered opinion. In general, we abide by this opinion, feeling that if we yet err, we err in good company.

To summarize the results of this editorial process, approximately one manuscript in ten is accepted as is, another one in ten is returned to the author as not suitable for this journal, and about eight in ten are accepted only after considerable revision based on the comments of informed readers. This process, incidentally, is similar to that of our sister journal, *J. Opt. Soc. Am.*

It frequently happens that a manuscript arrives which does not fall easily into any of the categories for which we have volunteer readers. In this case we scan the references of the article, and if the work seems to draw heavily from another author we send the manuscript to him for an opinion. Here we can sometimes go wrong, for unknown to us, each of these workers regards the other as a charlatan and the reader is of the opinion that this particular manuscript is but another fraud. Or else we innocently send the manuscript to a reader who was not listed among the references but who feels strongly that he should have been.

We have had other unusual experiences: For example, one author submitted a paper describing a marvelous breakthrough which deserved rapid publication, but he was applying for a patent and the paper could not appear until after a certain date. In the meantime he did not want anyone to read it who might have a proprietary conflict of interest. In such instances we have tried delicately to seek among our more trusted readers for one who would not grab this idea and run with it. (Fortunately we have several impractical friends who would not know how to run with any idea.) In a somewhat similar vein at least one author has argued that it is improper for us to show his manuscript, prior to publication, to any reader who might violate professional trust and show the manuscript to some of his associates. Our own interpretation would be that the legal priority and precedence of any idea embodied in a manuscript is established by the "Date Received" which the editorial staff promptly affixes to each paper as it comes in. This date would take priority over the date of appearance of the journal from the printers, and this date also antedates any subsequent ideas that the manuscript might generate in a referee's mind. This point is perhaps somewhat tricky, as the paper might fail of acceptance, in which case the readers did indeed have an advance look at someone else's idea, although just *what* it is in advance of is not quite clear. Refereeing a manuscript in one's own field should be regarded as a professional responsibility, and we see no intrinsic evil if a referee checks a disputed point with a colleague.

A substantial number of our critics feel we should not referee at all: just as every member of the Society has the right to present a paper at a meeting so should he also have the right to publish a paper. It is wrong, they say, when we have a controversial subject, to settle it outside the journal in letters between the author and an anonymous referee. This gives the referee a veto over every new idea. When the Editor or his umpire feels that the truth in a controversy lies someplace in between author and referee we have accepted the paper and invited the reviewer to rebut in print.

There are those who feel we should be much more severe on our papers; if we would only accept the one-tenth "best" papers we would be a much better journal and help hold under check the great upsurge of technical literature. If we pursue this point further with these critics we find that they feel the acceptable one-tenth really belongs in other journals anyway. This would certainly solve the problem.

JOHN N. HOWARD

HAVE YOU RENEWED YOUR SUBSCRIPTION?

The Effect of Extraneous Radiation on Photometric Accuracy of Infrared Spectrophotometers

James E. Stewart

Recent advances in infrared spectrophotometry have led to increased concern with the effects of radiation emitted by elements other than the source, for example, samples, reference beam attenuators, and the monochromator itself. Present levels of precision of measurement and purity of radiation are in some cases good enough that the effects of extraneous radiation can become significant, even with room temperature samples. Of particular interest are the areas of far-infrared spectroscopy, the study of very dense or highly reflecting samples, and the use of rotating sectors for photometric calibration. The magnitude of the expected effects of extraneous radiation will be discussed for several photometer systems, and the results of some experimental measurements will be described.

I. Introduction

The radiation detector of an infrared spectrophotometer is essentially a sensitive thermometer. It responds without discrimination to changes in temperature of objects in its field of view as well as to attenuation of radiation emitted by the spectrometer source. The early pioneers in infrared spectroscopy took elaborate precautions to fix the temperature of their instruments' surroundings. Coblentz[1] isolated his monochromator in an inner room and manipulated cells and shutters with a system of cables. He wrote of the necessity of remaining beside the instrument for some time until it adjusted to the temperature of his body before any measurements could be made. Indeed, this procedure was followed as recently as a decade ago by those of us who enjoyed the experience of operating dc spectrometers. The advent of instruments using chopped radiation and tuned amplifiers changed all this by permitting the selective detection of radiation which is modulated by the chopper. However, modern double-beam instruments are complicated systems incorporating rotating beam switchers and combiners, and it is often possible for extraneous radiation, as distinct from radiation generated by the spectrometer source, to be modulated and detected. Under some conditions this can contribute significant errors to photometric measurements. In this note, the magnitude of such errors will be estimated for several spectrophotometer systems. Particular attention will be paid to the use of the rotating sector because of the increasing use of this device in infrared photometric measurements.[2,3]*

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II. Equations for Radiation in a Spectrophotometer

The calculations to be discussed are really quite simple and will not be given in detail. The symbols used are defined in Table I, which deals with transmission, reflection, and emission by various spectrometer elements. The transmittance of attenuators or rotating sectors is given by f_c, f_w, or f_d, which are the geometric open fractions of these elements. The reflectance of attenuators is taken to be zero; the complicating effects of multiple reflectance in samples have been omitted, and the radiation emitted by the monochromator and reflected back into the monochromator is included. The power radiated by an element is the product of its emittance and the power which would be emitted by a blackbody at the same temperature. The emittance is given by Kirchhoff's law. For mathematical convenience, the radiant power which the element would emit if it were a blackbody is written as a fraction of the power radiated by the spectrometer source, G. For example, the power radiated by the sample is $(1 - T_S - R_S)sG$. The dependence of G on the wavelength and the temperature is given by the

* There is an error in Fig. 3 of ref. 2. The absorbtivity values reported for CaF_2 are defined in terms of base 10 logarithms, consistent with common chemical practice. The values given by Ballard *et al.* are defined in terms of base e logarithms and should have been multiplied by 0.434 before being plotted in Fig. 3. With this correction, they are seen to be in somewhat better agreement with our values.

Table I. Symbols and Definitions

Element	Transmittance	Reflectance	Emitted radiation
Sample, S	T_S	R_S	$E_S = (1 - T_S - R_S)sG$
Reference, R	T_R	R_R	$E_R = (1 - T_R - R_R)rG$
Reference beam attenuator, C	f_C	0	$E_C = (1 - f_C)cG$
Sample beam attenuator, W	f_W	0	$E_W = (1 - f_W)wG$
Atmosphere	T_a, T_a'	—	—
Shutter, B	0	R_B	$E_B = (1 - R_B)bG$
Spectrometer source, G	—	—	G
Monochromator, M	—	—	$E_M = mG$
Sector, D	f_D	$R_D(1 - f_D)$	$E_D = (1 - f_D)(1 - R_D)dG$
Chopper, F	—	R_F	$E_F = (1 - R_F)fG$

Planck radiation law. If the source is not a blackbody, G also depends on its emittance. The quantity s depends on the wavelength and on the temperature of both the source and the sample, but not on the emittance of the sample, which is given by $(1 - T_S - R_S)$. The power which would be emitted by a blackbody at the temperature of the sample is sG. Values of G, sG, rG, etc., are readily calculated from Planck's law for a given temperature and wavelength, or they can be found in tables.[4]

The examples discussed in the following sections are intended to be illustrative, and not exhaustive. The large number of conceivable combinations of instrumental parameters calls for simplification of the equations by means of "reasonable" assumptions. For example, the spectrometer source is taken to be at a temperature of 1600°K, which is often true of Nernst glowers, and to be a blackbody. We take 310°K for a reasonable monochromator temperature and 300°K for the temperature of the sample. Values of some of the parameters which occur frequently are tabulated in Table II. The effect of using sources of different temperatures is illustrated in Fig. 1, showing the radiant power emitted by a blackbody at 300°K relative to the power emitted by a source at 1000, 1300, and 1600°K.

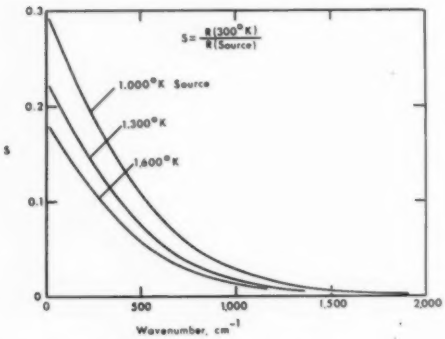

Fig. 1. The ratio, S, of radiant power emitted by a blackbody at 300°K, R (300°K) to radiant power emitted by blackbodies at 1000, 1300, and 1600°K, R (source).

III. Single-Beam Spectrophotometer

As a first example, let us consider a simple single-beam spectrophotometer, as illustrated in Fig. 2. If the chopper is placed at F_1, as it will be in the case of a single-pass monochromator, there will be no signal generated by extraneous radiation from samples, shutter, or monochromator. The chopper itself will either radiate, or reflect radiation originating elsewhere, but this cannot affect the measured transmittance of a sample.

In a double-pass monochromator the chopper is placed inside the monochromator at F_2. The ac signal obtained with sample, reference, or shutter in the beam is proportional to

$$J_S = GT_aT_a'T_S + E_ST_a' + E_MT_a'T_a''R_S - E_MT_a''', \quad (1)$$

$$J_R = GT_aT_a'T_R + E_RT_a' + E_MT_a'T_a''R_R - E_MT_a''', \quad (2)$$

or

$$J_0 = E_BT_a' + E_MT_a'T_a''R_B - E_MT_a''', \quad (3)$$

where T_a and T_a' refer to the transmittance of the atmosphere from source to sample and from sample to detector, respectively; T_a'' is the transmittance of the path between the sample and the emitting element of the monochromator (e.g., slit jaw), and T_a''' refers to the path between the chopper and the detector. The assumption is made that the chopper and the emitting element of the monochromator are nonreflecting and at the same temperature. The measured transmittance of the sample is

Table II. Values for m for 310°K and s for 300 and 298°K Relative to a 1600°K Source

ν (cm^{-1})	m (310°K)	s (300°K)	s (298°K)
50	0.1761	0.1697	0.1684
100	0.1593	0.1529	0.1516
200	0.1288	0.1224	0.1212
400	0.0802	0.0746	0.0734
500	0.0619	0.0568	0.0558
700	0.0355	0.0317	0.0309
1000	0.0143	0.0122	0.0118
1500	0.0028	0.0021	0.0020
2000	0.0005	0.0003	0.0003

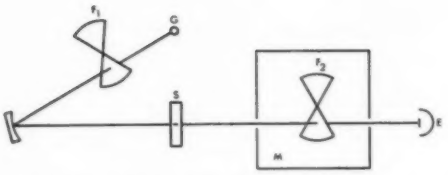

Fig. 2. Schematic drawing of the optical path of a single-beam spectrophotometer. Radiation from the source G is chopped either by F_1 before passing through the sample S, or by F_2 in the monochromator M before being detected at E.

$$T_{app} = \frac{J_S - J_0}{J_R - J_0} =$$

$$\frac{T_S(T_a - s) + (1 - R_S)s + m(R_S - R_B)T_a'' - b(1 - R_B)}{T_R(T_a - r) + (1 - R_R)r + m(R_R - R_B)T_a'' - b(1 - R_B)}. \quad (4)$$

In the highly probable case of sample, reference, and shutter all at the same temperature, $s = r = b$, and Eq. (4) becomes

$$T_{app} = \frac{T_S(T_a - s) + (R_S - R_B)(mT_a'' - s)}{T_R(T_a - s) + (R_R - R_B)(mT_a'' - s)} \quad (4a)$$

and if in addition neither the reference nor the shutter is reflecting

$$T_{app} = \frac{T_S}{T_R} + \frac{R_S(mT_a'' - s)}{T_R(T_a - s)}. \quad (4b)$$

The error in T is largest for highly reflecting samples. For example, a measurement of the transmittance of a semiconductor sample at 400 cm^{-1} can be 0.4% T too high (taking $T_R = 1$, $R_S = 64\%$, $T_S = 36\%$, $T_a = T_a' = 1$, and m and s corresponding to 310 and 300°K, respectively).

However, if a highly reflecting shutter is used, $R_B = 1$,

$$T_{app} = \frac{T_S(T_a - s) + (R_S - 1)(mT_a'' - s)}{T_R(T_a - s) - (mT_a'' - s)} \quad (4c)$$

and the apparent transmittance of the sample is measured without error. On the other hand, a sample of zero reflectance will be measured correctly when using a black shutter and will have an indicated transmittance which is too low when a reflecting shutter is used.

IV. Double-Beam Spectrophotometers of the IR-4 Type

The photometer optics of IR-4 type spectrometers are arranged in a "box" configuration (see Fig. 3) with two rotating mirrors to separate and recombine the beams. The ac radiant power seen by the detector through the sample beam is proportional to

$$J_S = GT_aT_a'T_Sf_W + E_Sf_WT_a' + E_WT_a' + E_MT_a'^2f_WR_S. \quad (5)$$

Similarly, for the reference beam

$$J_R = GT_a'T_aT_Rf_c + E_cT_RT_a + E_RT_a + E_MT_a^2R_R. \quad (6)$$

The instrument is servo balanced to make $J_S = J_R$ by positioning the reference beam attenuator:

$$f_c = [T_ST_a'f_W(T_a - s) + R_ST_a'f_W(mT_a' - s) + T_RT_a(r - c) + R_RT_a(r - mT_a) + f_WT_a'(s - w) + wT_a' - rT_a]/T_RT_a(T_a' - c). \quad (7)$$

This equation will be simplified by taking $f_W = 1$.

The three important types of error in double-beam spectrophotometry are zero errors, transmittance errors, and compensation errors.

A. Zero Errors

If the sample is opaque, the reference neither reflecting nor absorbing, and the spectral region free of atmospheric absorption, we find a zero error

$$f_c^0 = \frac{R_S(m - s) - (c - s)}{1 - c} \quad (8)$$

originating in temperature differences between the monochromator and the sample and between the reference beam attenuator and the sample. The latter is seen to be a negative error for the usual case of the attenuator hotter than the sample, and can give a falsely optimistic measure of stray radiation. If the attenuator is 10° hotter than a nonreflecting sample, this error can amount to 0.8% at 50 cm^{-1}, 0.4% at 700 cm^{-1}, and 0.2% at 1000 cm^{-1} (from Table II). If a highly reflecting shutter is used to establish zero, it introduces an error opposing the contribution of the attenuator, and the two cancel each other for equal attenuator and monochromator temperatures. On the other hand, if the attenuator and shutter are at the same temperature, use of highly reflecting shutters will introduce positive zero errors of the same magnitude as those cited above for a hot attenuator and nonreflecting sample.

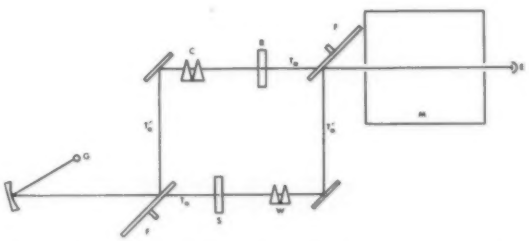

Fig. 3. Schematic drawing of the optical path of a double-beam optical-null spectrophotometer of the *IR*-4 type. Radiation from G is diverted alternately to the sample S and reference R, and then recombined and sent to the monochromator M and detector E by the rotating elements at F. The reference beam attenuator C equalizes the radiant power transmitted by the two beams, and the sample beam attenuator W is used to adjust the 100% level. T_a and T_a' refer to transmittance by atmospheric constituents distributed along the paths before and after S and R. In the text S and R are assumed to be very close to W and C.

Table III. Expected Compensation Errors, Δf_c

T_S^0 (%)	Δf_c (%)[a]	Δf_c (%)[b]
100	0	0
50	0.08	0.11
10	0.68	0.96
5	1.43	2.03
1	7.46	10.59

[a] A 2°K temperature difference between a sample and an identical reference of transmittance T_S^0.

[b] A strong atmospheric band having $T_a = 0.90$ and $T_a' = 0.92$. Both cases are based on nonreflecting samples at 300°K, observed at 700 cm^{-1} using a 1600°K source.

B. Transmittance Errors

In a spectral region where $T_a = T_a' = 1$ we have

$$f_c = \frac{T_S(1-s) + R_S(m-s) - T_R(c-r) - R_R(m-r) + (s-r)}{T_R(1-c)}. \quad (9)$$

If the reference neither reflects nor absorbs and the sample, reference, and attenuator are at the same temperature ($s = r = c$), this expression takes the form

$$f_c = T_S + \frac{m-s}{1-s} R_S. \quad (9a)$$

If $s = r$ and $m = c$, it takes the form

$$f_c = T_S \frac{(1-s)}{(1-m)} - \frac{(m-s)}{(1-m)}(1 - R_S). \quad (9b)$$

The dependence of transmittance errors on sample reflectance in the two cases is different.

C. Compensation Errors

When the sample and reference beams of a double-beam spectrophotometer contain identical absorbers, the balance position of the reference beam attenuator should not depend on their transmittance. Failure to meet this condition is termed compensation error. We can consider two classes of compensation error depending on whether we are interested in canceling absorption by identical components of the sample and reference materials confined to cells in both beams or in canceling absorption by a substance distributed along the beams, such as atmospheric water vapor.

First, consider a spectral region free of atmospheric absorption, $T_a' = T_a = 1$, and write the transmittance and reflectance of sample and reference

$$T_S = T_S^0 - \delta T_S, \qquad T_R = T_S^0, \qquad R_S = R_R.$$

The reference beam attenuator will be balanced at

$$f_c = 1 - \frac{T_S^0 + R_S - 1}{T_S^0}\left(\frac{s-r}{1-c}\right) - \frac{\delta T_S}{T_S^0}\left(\frac{1-s}{1-c}\right). \quad (10)$$

If the sample and reference materials are at the same temperature, then, depending on the relative temperatures of the sample, attenuator, and monochromator,

$$f_c = 1 - \frac{\delta T_S}{T_S^0}, \qquad s = r = c, \quad (10a)$$

or

$$f_c = 1 - \frac{\delta T_S (1-s)}{T_S^0 (1-m)}, \qquad s = r, \qquad c = m. \quad (10b)$$

There is no compensation error in (10a). In (10b) the compensation error is very slight for $\delta T_s \ll T_s^0$. If the sample and reference materials are not at the same temperature, there is an additional error,

$$\frac{1 - T_S^0 - R_S}{T_S^0}\left(\frac{s-r}{1-c}\right).$$

The favorable signal-to-noise ratio of modern instruments permits differential analysis in quite dense media. Under such conditions the compensation error can become large, as shown by the calculated values in Table III.

Now consider a region in the spectrum where the atmosphere absorbs, but assume that the sample and reference are identical and at the same temperature. The attenuator will be positioned at

$$f_c = 1 - \frac{1 - T_S}{T_S}\frac{s(T_a - T_a')}{T_a(T_a' - c)} + R_S \frac{s(T_a - T_a') - m(T_a^2 - T_a'^2)}{T_S T_a (T_a' - c)}. \quad (11)$$

For a "symmetric" photometer design having four equal path segments and the same vapor pressure of atmospheric absorber in all segments, this equation reduces to $f_c = 1$. In actual spectrometers utilizing this design neither condition is usually met, particularly if the monochromator and photometer housings, but not the sample area, are flushed with dried air. The error is dependent on sample transmittance and reflectance and becomes large when dense samples are studied. Some calculated compensation errors are given in Table III.

D. Single-Beam Operation

In single-beam operation of an IR-4 type spectrophotometer, the reference beam is blocked with an opaque shutter. The amplitude of the ac signal generated by the detector is proportional to

$$J = J_S - J_R = GT_aT_a'T_S + E_ST_a' + E_MT_a'^2R_S - E_BT_a - E_MT_a^2R_B. \quad (12)$$

If there is no atmospheric absorption and no temperature differences between sample and reference beam blocker, this equation reduces to

$$\frac{J}{G} = T_S(1-s) + (R_S - R_B)(m-s). \quad (12a)$$

The zero transmittance level is established by inserting a shutter of reflectance R_B' in place of the sample, and the 100% transmittance level might be taken as the

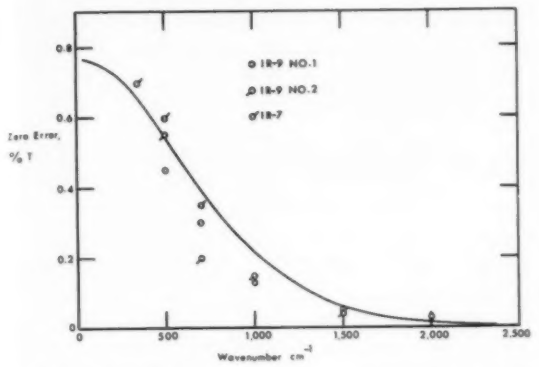

Fig. 4. Zero error of an IR-4 type spectrophotometer in single-beam operation calculated for a perfectly reflecting, opaque sample at 300°K with a 310°K monochromator and a 1600°K source. The experimental points were determined with a black shutter blocking the reference beam by comparing the apparent transmittance of a black opaque shutter and a highly reflecting opaque shutter.

signal obtained with an empty sample beam. The apparent transmittance of a sample, taking $R_B = R_B' = 0$, is

$$T_{\text{app}} = T_S + R_S \frac{(m - s)}{(1 - s)}. \tag{13}$$

T_{app} contains a zero error ranging from 0 to $(m - s)/(1 - s)$ depending on the reflectance of the sample. Figure 4 shows a curve of $(m - s)/(1 - s)$ for an assumed source temperature of 1600°K, a sample temperature of 300°K, and a monochromator temperature of 310°K. The experimental values plotted in Fig. 4 were obtained by measuring the apparent transmittance of a black shutter and a highly reflecting shutter, using two Beckman IR-9's and an IR-7 with a far infrared interchange. The measured values agree very well with the calculated curve, in view of the assumptions made.

It is customary to measure stray radiation* in a monochromator by determining the apparent transmittance of a sample at a frequency where it is opaque. The 700 cm^{-1} band of polystyrene is useful for this purpose. In the presence of stray radiation the apparent transmittance of an opaque sample is, from Eq. (13),

$$T_0^{(1)} = \frac{R_S(m - s) + S}{1 - s + S}, \tag{14}$$

where S is the relative level of stray radiation in the monochromator. It is assumed that the presence of the sample does not alter the magnitude of stray radiation reaching the detector. If $R_S = 0$, and S is not too large, $T_0^{(1)}$ is very nearly equal to S. However, R_S may become appreciable in the vicinity of a very strong absorption band, leading to an erroneously high value for stray radiation.

If the sample beam is blocked, however, with the sample still in place between the shutter and the monochromator, a different apparent transmittance

$$T_0^{(2)} = \frac{R_S(m - s)}{1 - s + S} \tag{15}$$

is observed. The difference between these values, $\Delta = T_0^{(1)} - T_0^{(2)}$, is a much better measure of stray radiation, for

$$S = \frac{\Delta(1 - s)}{1 - \Delta} \approx \Delta. \tag{16}$$

Observed and calculated values are compared below for a Beckman IR-4, assuming a 25% reflecting sample measured at 700 cm^{-1} and 0.1% stray radiation.

	Observed	Calculated
$T_0^{(1)}$	0.0021	0.0020
$T_0^{(2)}$	0.0009	0.0010
Δ	0.0012	—

V. Double-Beam Spectrophotometers of Other Types

Some infrared spectrophotometers have photometer optics arranged in the configuration shown schematically in Fig. 5. The reference and sample beams are split optically and recombined with a rotating mirror. The reference beam attenuator may be placed at (C_I) (example: Beckman IR-5) or at (C_{II}) (example: Perkin-Elmer 21). The radiant power observed through the sample beam is given by (5) in case II and by

$$J_S^{\text{I}} = GT_aT_a'f_WT_S + E_ST_a' + E_WT_ST_a' + E_MT_a'^2R_S \tag{5a}$$

in case I. The reference beam power is

$$J_R^{\text{I}} = GT_aT_a'T_Rf_c + E_cT_RT_a' + E_RT_a' + E_MT_a'^2R_R \tag{17}$$

and

$$J_R^{\text{II}} = GT_aT_a'T_Rf_c + E_cT_a' + E_RT_a'f_c + E_MT_a'^2f_cR_R \tag{18}$$

in the two cases. The equation governing the position of the reference beam attenuator for case I is

$$f_c^{\text{I}} = \{T_S[f_W(T_a - w) + w - s] + R_S(mT_a' - s) + T_R(r - c) + R_R(r - mT_a') + s - r\}/T_R(T_a - c), \tag{19}$$

and for case II

$$f_c^{\text{II}} = \frac{T_Sf_W(T_a - s) + R_Sf_W(mT_a' - s) + f_W(s - w) + (w - c)}{T_R(T_a - r) - R_R(r - mT_a') - (c - r)}. \tag{20}$$

When working in a region free of atmospheric absorption, with a nonabsorbing, nonreflecting reference material and with the sample beam attenuator withdrawn, f_c, f_c^{I}, and f_c^{II} are identical.

* Radiation of a wavelength which is remote from the nominal wavelength setting of the monochromator, but which falls on the detector

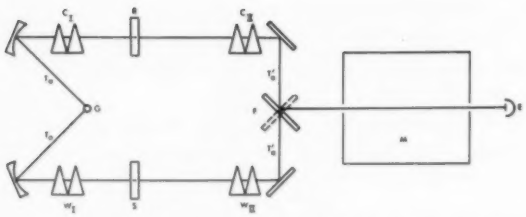

Fig. 5. Schematic drawing of the optical path of a double-beam optical-null spectrophotometer of the IR-5 type (attenuators at C_I and W_I) or the Model 21 type (attenuators at C_{II} and W_{II}). The beams are recombined by a rotating element at F.

VI. Rotating Sector Attenuators

Rotating sector attenuators[2] can be constructed in such a way that transmittance can be varied from $^1/_2$ to 0. They offer a convenient method for calibration of spectrophotometers. It is known that under some conditions thermal emission from these devices can affect their apparent transmittance. Indeed, Coblentz,[1] in describing the transmittance of rotating sectors measured on his infrared spectrophotometer in 1908, writes of "high values due to radiation from the moving disk". In this section, we discuss the significance of this limitation. The treatment is limited to IR-4 type spectrophotometers, operating in single- and double-beam modes, but extension to other classes of spectrophotometer is easy.

A. Single-Beam Operation

Proceeding as in Section IV.D, and assuming that $T_a = T_a' = 1$ and that the reference beam shutter has the same reflectance and temperature as the blades of the sector, we find an equation analogous to (12a):

$$(J/G)_{\text{sector}} = f_D[(1 - d) - R_D(m - d)]. \quad (21)$$

With the sector removed from the beam, the radiant power detected is

$$(J/G)_{100} = (1 - d) - R_D(m - d). \quad (22)$$

Hence, the apparent transmittance of the sector is

$$T_{\text{app}} = \frac{(J/G)_{\text{sector}}}{(J/G)_{100}} = f_D \quad (23)$$

and there is no error.

An experimental test of this conclusion was made using a 45% transmitting rotating sector with nonreflecting blades in an IR-9. Apparent transmittance values measured at a series of wavenumbers between 500 and 2000 cm^{-1} agreed within a standard deviation of 0.1% T, with no wavenumber dependence.

B. Double-Beam Operation

If a rotating sector is placed in the sample beam of an IR-4 we have

$$\frac{J_S}{G} = f_D + (1 - f_D)(1 - R_D)d + mR_D(1 - f_D). \quad (24)$$

With a reference beam free of absorbing and reflecting material, the balance condition is

$$f_e = \frac{f_D[(1 - d) - R_D(m - d)] + (d - c) + R_D(m - d)}{(1 - c)}. \quad (25)$$

There is no error provided that the sector is at the same temperature as the reference beam attenuator and $R_D = 0$, or that the reference beam attenuator is at the same temperature as the monochromator and $R_D = 1$. Moreover, the occurrence of a zero error is not serious as the zero level is established with the sector closed.

An experimental test of a rotating sector in an IR-9 operated double-beam verified that there is no wavelength dependence of apparent transmittance between 500 and 2000 cm^{-1}, within a standard deviation of 0.16% T.

A rotating sector can be used as a reference beam attenuator in place of the usual comb, in the manner described in ref. 3. The equation describing the setting of f_D for balance of the two beams is the same as Eq. (7), with appropriate interchange of subscripts. In this case photometric errors accompanying extraneous emission will occur, to the same extent as the errors discussed in Section IV.

VII. Conclusion

The photometric errors which are associated with extraneous emission are generally small except at long wavelengths. Until very recently they would have been considered negligible in comparison with other sources of error. Modern infrared spectrophotometers have quite low stray radiation and offer favorable signal-to-noise ratios, permitting extreme scale expansion and spectrophotometry of optically dense materials. Moreover, many laboratories are interested in measuring the optical properties of hot samples. Under these circumstances the errors due to extraneous radiation can become serious. In the event that the errors become intolerable it is often possible to avoid them by a simple modification of the spectrophotometer. The rotating element which recombines the sample and reference beams can be replaced with a nonchopping element[2] (e.g., a strip mirror) at the cost of about half of the useful radiation.

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Lattice Vibration Spectra of $Mg(OH)_2$ and $Ca(OH)_2$

R. A. Buchanan, H. H. Caspers, and J. Murphy

The infrared absorption spectra from 700 to 75 cm^{-1} of $Mg(OH)_2$, $Mg(OD)_2$, $Ca(OH)_2$, and $Ca(OD)_2$ are presented. These spectra were obtained from powders dispersed in polyethylene. In addition, the results of a Raman scattering experiment performed on a single crystal of $Mg(OH)_2$ are presented. These results indicate four lines corresponding to the four predicted symmetric modes. The results of these experiments are compared with previous data obtained from other Raman and inelastic neutron scattering experiments to determine fundamental lattice vibrations of these crystals. Many of these lattice vibrations are observed to combine with the OH^- stretching vibrations to produce the complex absorption spectra near 2.7 μ.

Introduction

The infrared absorption spectra of the mineral brucite $Mg(OH)_2$ have perplexed investigators since Coblentz[1] published the first spectrum in 1905. It seems appropriate that a paper dealing with this problem, opened by Coblentz 58 years ago, be included in the Coblentz commemorative issue of the journal *Applied Optics*.

Subsequent to Coblentz' work, infrared spectra of $Mg(OH)_2$ were published by Plyler,[2] Randall and Nielsen,[3] Ta,[4] Louisfert,[5] Keller and Pickett,[6] Mara and Sutherland,[7] and Mitra.[8]

The complex nature of the absorption spectrum of $Mg(OH)_2$ in the OH^- stretching region (2.7 μ) caused Mara and Sutherland[7] to question the validity of the crystal structure determinations since only one infrared active OH^- stretching fundamental was allowed by crystal symmetry. The crystal structure was redetermined by Petch and Megaw[9] to be D_{3d}^3 ($P\bar{3}m$) as had been established by earlier workers.[10-16] Nuclear magnetic resonance spectra[17] confirmed the x-ray crystal structure and determined the proton positions. Mara and Sutherland reinvestigated the absorption spectra at liquid nitrogen temperature and found that the intensities of certain bands were very temperature-dependent. They were thus able to conclude that the complex structure in the 2.7-μ region of the $Mg(OH)_2$ absorption spectrum was due primarily to combination bands.

Hexter and Dows[18] next suggested that these combination bands were due to a coupling of librational OH^- modes to the OH^- stretching fundamental. Based on their theory, they predicted the fundamental libration mode of $Mg(OH)_2$ to occur at about 400 cm^{-1}. Hexter[19] developed the libration theory further and applied it specifically to $Mg(OH)_2$ and to the isomorphous mineral portlandite, $Ca(OH)_2$. The crystal structure of $Ca(OH)_2$ is D_{3d}^3 ($P\bar{3}m$). The neutron diffraction study of Busing and Levy[20] indicates the proton positions to be in agreement with the $Mg(OH)_2$ structure. This study also predicted the OH^- libration mode to be about 350 cm^{-1}. The infrared absorption spectrum of $Ca(OH)_2$ in the 2.7-μ region has been studied by Mara,[7(b)] Petch and Megaw,[21] and by Morgan and Busing[22] and is very similar to that of $Mg(OH)_2$. The Raman spectrum of $Ca(OH)_2$ has also been reported.[23,24]

Wickersheim[25] reported that the absorption spectra of LiOH also exhibit combination bands in the fundamental OH^- stretching region (2.7 μ). He analyzed the spectra from the point of view that generalized lattice vibrations rather than localized librations were combining with symmetric (Raman) and antisymmetric (infrared) OH^- stretching vibrations to produce the observed combination bands. Subsequent publications[26-29] dealing with the absorption spectra of LiOH and LiOD indicate that some disagreement still exists regarding the best model to use in order to interpret the combination band spectra.

Both the localized libration model and the lattice vibration model assume that resonances in the 100 to 700 cm^{-1} region are combining with the OH^- stretching frequency to give rise to the combination bands observed in the 2.7-μ region. It is the purpose of this article to present the infrared absorption spectra of $Mg(OH)_2$, $Mg(OD)_2$, $Ca(OH)_2$, and $Ca(OD)_2$ in the 100 to 700 cm^{-1} spectral region. In addition, the Raman spectrum of $Mg(OH)_2$ has been obtained, using the

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Applied Physics Corporation Cary Model 81 Raman spectrophotometer. This new data make possible a comparison of the lattice mode frequencies of $Mg(OH)_2$ and $Ca(OH)_2$. Results from a recent study[30] of the inelastic scattering of slow neutrons from $Mg(OH)_2$ and $Ca(OH)_2$ will also be compared with the infrared and Raman data. The lattice mode frequencies, as determined by the infrared and Raman data, will be observed to account for many of the combination bands in the 2.7-μ region.

Experimental

The infrared absorption of most ionic crystals is so very intense that it is difficult and sometimes impossible to prepare single crystal samples thin enough to get radiation through them at the wavelengths of maximum absorption. In order to get around this problem powders of the materials to be studied were dispersed in a polyethylene matrix. This technique suffers from the fact that polarization data are lost. Polyethylene has no absorption bands in the spectral region of interest. This technique for taking infrared spectra was suggested by Yoshinaga and Oetjen.[31] A similar method was developed by Yamada *et al.*[32] for preparing far-infrared transmission filters. The details of the sample preparation technique used in this study are presented elsewhere.[33]

The powders of $Mg(OH)_2$ and $Mg(OD)_2$ were prepared by reacting either H_2O or D_2O with magnesium nitride according to the following reaction:

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3\uparrow$$

The powder was dried in vacuum and used immediately to make the samples. Powders of $Ca(OH)_2$ were prepared by reacting calcium metal directly in H_2O or D_2O. The resultant powder precipitate was dried in vacuum and used immediately to make the samples.

The spectra were obtained by using a Beckman IR-7 with CsI grating interchange unit in the spectral region 700 to 225 cm^{-1}. A modified Perkin-Elmer 98 monochromator was used to obtain the spectra from 250 to 75 cm^{-1}.

The spectra are presented in Fig. 1. The correspondence between $Mg(OH)_2$ and $Ca(OH)_2$, as well as between $Mg(OD)_2$ and $Ca(OD)_2$, is almost perfect. In $Mg(OH)_2$ two strong absorption bands at 368 and 450 cm^{-1} dominate the spectrum. The corresponding bands in $Ca(OH)_2$ appear at 315 and 390 cm^{-1}.

The prominent change upon deuteration is the appearance of a new band at 310 cm^{-1} in $Mg(OD)_2$ and 265 cm^{-1} in $Ca(OD)_2$. The analogous bands in $Mg(OH)_2$ and $Ca(OH)_2$ are somewhat ambiguous. However, in $Ca(OD)_2$ the 390 cm^{-1} band seems to be slightly less intense than in $Ca(OH)_2$. This weakly suggests that the 390 cm^{-1} band in $Ca(OH)_2$ has shifted to 265 cm^{-1} in $Ca(OD)_2$ and, in so doing, uncovers another band near 410 cm^{-1}. In $Mg(OD)_2$ the 310 cm^{-1} band probably shifted from the 450 cm^{-1} region in $Mg(OH)_2$.

Discussion

The group theoretical predictions of the number and type of factor group ($\mathbf{k} = 0$) modes which will occur in $Mg(OH)_2$ and $Ca(OH)_2$ have been worked out.[8,26,34] These modes are summarized in Table I. It is noted that all the modes are either infrared or Raman active.

Observed frequencies of $Mg(OH)_2$ and $Ca(OH)_2$ are summarized in Tables II and III. The combination bands near 2.7 μ have been omitted from these tables and will be considered separately.

The 135 cm^{-1} band in $Mg(OH)_2$ and the 83 cm^{-1} band in $Ca(OH)_2$, observed in inelastic neutron scattering, were assigned by their discoverers as due to an acoustic branch. These bands do not appear in either the infrared or the Raman spectra, and hence their assignment is in agreement with these results.

The 310 cm^{-1} band in $Mg(OD)_2$ and the 265 cm^{-1} band in $Ca(OD)_2$ are not present in the $Mg(OH)_2$ and $Ca(OH)_2$, and consequently are assigned as the $E_u(R)$ modes (see Table I). If the rocking and translation E_u modes do not mix significantly, then the former should appear at approximately $310 \times (17/9)^{1/2} = 426$ cm^{-1} in $Mg(OH)_2$ and $270 \times (17/9)^{1/2} = 371$ cm^{-1} in $Ca(OH)_2$. These modes appear to be merged in the broad absorption regions centered about 450 cm^{-1} in $Mg(OH)_2$ and 390 cm^{-1} in $Ca(OH)_2$. The fact that strong absorption remains in the 450 cm^{-1} and 390 cm^{-1} regions in $Mg(OD)_2$ and $Ca(OD)_2$, respectively, implies possibly an accidental degeneracy of the $E_u(R)$ modes in $Mg(OH)_2$ and $Ca(OH)_2$ with translational modes $E_u(T)$ or $A_{2u}(T)$ which do not shift significantly upon deuteration.

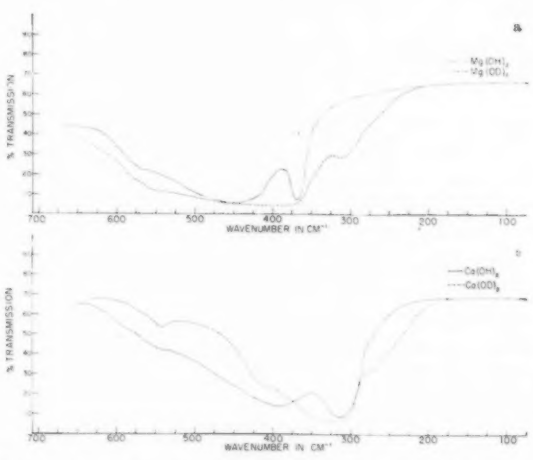
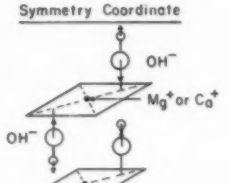
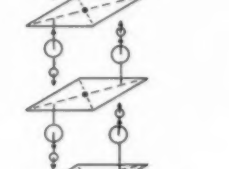
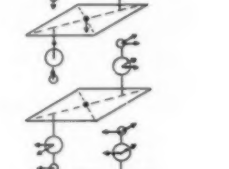
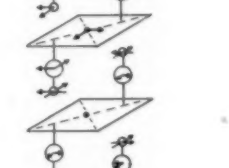
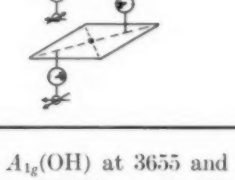
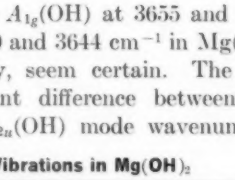
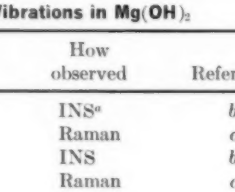
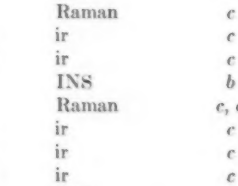


Fig. 1. (a) Absorption spectra of $Mg(OH)_2$ and $Mg(OD)_2$ powders dispersed in polyethylene. (b) Absorption spectra of $Ca(OH)_2$ and $Ca(OD)_2$ powders dispersed in polyethylene.

Table I. Symmetry Coordinates for Unit Cell Modes of $Mg(OH)_2$ and $Ca(OH)_2$

Species	Activity	Symmetry Coordinate
A_{1g} (OH)	Raman	
A_{2u} (OH)	Infrared	
A_{1g} (T)	Raman	
A_{2u} (T)	Infrared	
E_g (T)	Raman	
E_u (T)	Infrared	
E_u (R)	Infrared	
E_g (R)	Raman	

The assignments of the A_{1g}(OH) at 3655 and 3618 cm^{-1} and A_{2u}(OH) at 3700 and 3644 cm^{-1} in Mg(OH) and $Ca(OH)_2$, respectively, seem certain. The fact that there is a significant difference between the A_{1g}(OH) mode and the A_{2u}(OH) mode wavenumbers is clear evidence for some coupling between the internal vibrations of the OH^- ions in these crystals.

Table II. Lattice Vibrations in $Mg(OH)_2$

$Mg(OH)_2$ (cm^{-1})	$Mg(OD)_2$ (cm^{-1})	How observed	Reference
135 ± 10		INS[a]	*b*
250		Raman	*c*
281 ± 9		INS	*b*
282		Raman	*c*
	310 ± 10	ir	*c*
368 ± 5	368 ± 20	ir	*c*
377 ± 8		INS	*b*
445		Raman	*c, d*
450 ± 15	450 ± 50	ir	*c*
565 ± 20	550 ± 20	ir	*c*
	575 ± 20	ir	*c*
633 ± 30		INS	*b*
3655		Raman	*c, d*
3700	2721	ir	*d*

[a] INS—Inelastic neutron scattering.
[b] See ref. 30.
[c] Results from present investigation.
[d] See ref. 8.

Table III. Lattice Vibrations Observed in $Ca(OH)_2$

$Ca(OH)_2$ (cm^{-1})	$Ca(OD)_2$ (cm^{-1})	How observed	Reference
83 ± 7		INS[a]	*b*
247 ± 15		INS	*b*
247		Raman	*c*
	265 ± 30	ir	*d*
282		Raman	*c*
315 ± 5	315 ± 20	ir	*d*
316 ± 7		INS	*b*
359		Raman	*c*
390 ± 15		ir	*d*
	410 ± 20	ir	*d*
540 ± 20	540 ± 10	ir	*d*
540 ± 30		INS	*b*
3618		Raman	*e*
3644	2688	ir	*f*

[a] INS—Inelastic neutron scattering.
[b] See ref. 30.
[c] See ref. 24.
[d] Results from present investigation.
[e] See ref. 23.
[f] See ref. 22.

The combination bands of x, y polarization in $Mg(OH)_2$ and $Ca(OH)_2$ are summarized in Tables IV and V. The combination band frequencies are computed by dividing their separation into two equal parts. The dividing line is seen to correspond quite well with either the Raman or infrared OH^- stretching wavenumber. The wavenumbers for the combination modes, computed in this way, agree remarkably well with the observed lattice vibration wavenumbers. This agreement supports the contention that lattice vibrations are coupling to the stretching fundamentals to produce combination bands in $Mg(OH)_2$ and $Ca(OH)_2$.

The combination bands used in Tables IV and V are x, y polarized combination bands. Mitra's data[8] for $Mg(OH)_2$ include the z polarization as well as the x, y polarization, but no agreement with observed lattice vibrations is obtained for the z polarized combination bands.

Table IV. Combination Band Assignments in $Mg(OH)_2$

Combination bands[a] (cm^{-1})	Center[b] (cm^{-1})	Combination[c] (cm^{-1})	Lattice vibration (cm^{-1})
3790 − 3534	3662	128	135 ± 10 acoustic branch, INS
3956 − 3448	3702	254	250 Raman
3956 − 3368	3662	294	282 INS, Raman
4042 − 3270	3656	386	368 ± 5 INS, ir
4316 − 3025	3670	645	282 + 368 = 650

[a] Data taken from Mitra.[8]
[b] Sum of combination bands (cm^{-1}) ÷ 2.
[c] Difference of combination bands (cm^{-1}) ÷ 2.

Table V. Combination Band Assignments in $Ca(OH)_2$

Combination bands[a] (cm^{-1})	Center[b] (cm^{-1})	Combination[c] (cm^{-1})	Lattice vibration (cm^{-1})
3720 − 3523	3622	99	83 ± 7 acoustic branch, INS
3877 − 3364	3620	256	247 ± 15 Raman, INS
3899 − 3333	3616	283	282 Raman
3932 − 3294	3613	319	315 ± 5 ir, INS
4164 − 3073	3618	545	247 + 315 = 562

[a] Data from Morgan and Busing.[22]
[b] Sum of combination band (cm^{-1}) ÷ 2.
[c] Difference of combination band (cm^{-1}) ÷ 2.

The infrared reflection spectrum of $Mg(OH)_2$ has been analyzed with dispersion relations by Mitra[35] to obtain values for the peaks of the absorption. The values which he reports are 460 cm^{-1} (unpolarized) and 380 cm^{-1} (x, y polarized). The former value is in excellent agreement with the value 450 ± 15 cm^{-1} found in the present investigation. The correlation of the latter value with the value of 368 ± 5 cm^{-1} found in the present investigation also seems certain, although the wavenumber agreement is not as good.

The complete explanation of the combination band spectrum in the 2.7-μ region in $Mg(OH)_2$ and $Ca(OH)_2$ must await a complete knowledge of the lattice vibrations including the $\mathbf{k} \neq 0$ modes.

Summary

Lattice modes of propagation vector near $\mathbf{k} = 0$ have been observed in the infrared and Raman spectra of $Mg(OH)_2$ and $Ca(OH)_2$. The frequencies of these modes are compared with frequencies obtained by inelastic neutron scattering experiments, and the agreement is good. The frequencies of these lattice modes are observed in combination with the frequencies of the internal OH^- stretching vibrations near 2.7 μ. It is, therefore, concluded that lattice vibrations near $\mathbf{k} = 0$ can and do couple to produce at least some of the combination bands observed near 2.7 μ. The acoustic branch maximum frequency as observed by inelastic neutron scattering experiments is also observed in combination with the OH^- internal vibrations. It seems reasonable to assume that the combination bands not accounted for by $\mathbf{k} = 0$ lattice vibrations may be associated with $\mathbf{k} \neq 0$ lattice vibrations.

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A New Standard of Spectral Irradiance

Ralph Stair, William E. Schneider, and John K. Jackson

The National Bureau of Standards has made available a new standard of spectral irradiance in the form of a 200-W quartz-iodine lamp with a coiled-coil tungsten filament operating at about 3000°K and calibrated over the spectral range of 0.25 to 2.6 μ. The calibration of this standard is based upon the radiance of a blackbody as defined by the Planck law of radiation, since it was done by comparisons with the NBS standards of spectral radiance, of luminous intensity, and of total irradiance, each of which was established through the use of blackbodies. This standard is used without auxiliary optics. Because of its small physical size and high operating temperature, relatively high spectral irradiances may be obtained through its use.

I. Introduction

The precise measurement of irradiance from a source requires the use of a calibrated detector or a calibrated source which may be employed in a transfer calibration. The need for a calibrated source was originally met by Coblentz[1] in 1914 with the development of a carbon filament standard of total irradiance. Calibration and use of this type of standard have been subsequently reported by Coblentz and other personnel of the NBS Radiometry Laboratory.[2-4] Accurate calibration with this type of standard requires a detector with a nonselective spectral response. A thermopile heavily coated with dull lampblack or carbon black meets this requirement reasonably well from the near ultraviolet through the visible and near infrared portions of the spectrum. However, the relatively low sensitivity of thermopiles and other thermal detectors together with the fact that they are not entirely nonselective spectrally makes their use difficult for the evaluation of the spectral distribution of radiant flux.

Considerable work has been done on the emissivity of tungsten ribbon and wire filament lamps,[5-11] and, coupled with measurements of temperature, an approximate standard of spectral radiance or of spectral irradiance can be set up. A number of laboratories including the National Bureau of Standards have followed this procedure.[12-17] In 1960, the National Bureau of Standards developed a standard of spectral radiance[18] in the form of a tungsten ribbon-filament lamp calibrated by direct comparison with a blackbody, the spectral radiance of which is computed from Planck's radiation equation. These lamp standards have found wide use in the calibration of spectroradiometric and other equipment in which a small area, like a slit, is to be irradiated. However, the use of this standard is limited by the small area which can be irradiated, by the low irradiance which the standard provides in the ultraviolet, and by the auxiliary optics required. For many types of spectroradiometric calibration, a standard of spectral radiance has been found to be very useful and will no doubt continue to be useful. However, in many cases, a standard of spectral irradiance is needed. To fulfill this need and to provide a source of higher irradiance in the ultraviolet, a new standard of spectral irradiance has been developed.

II. Apparatus and Method

Before proceeding with the establishment of a standard of spectral irradiance for the region of 0.25 to 2.6 μ based upon the radiance of a blackbody at a known temperature, we made a study of possible lamp designs. First thought was given to the specially constructed tungsten-in-quartz lamp previously employed in this laboratory[12,13] as a standard of spectral irradiance based upon color temperature and the published spectral emissivity data for tungsten. It was recognized that this lamp had three principal deficiencies: its low operating temperature, poor optical quality and bulkiness of the quartz envelope, and relatively large filament area. Only very low ultraviolet irradiances could be realized at a spectrometer slit. Also, since each tungsten filament differs somewhat in emissivity as a function of its specific shape and surface condition,

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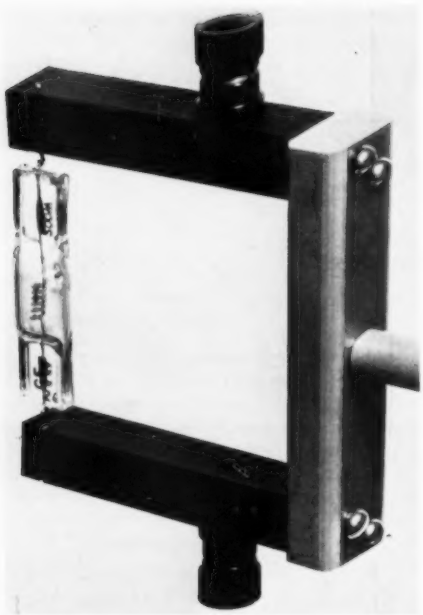

Fig. 1. Quartz-iodine lamp standard of spectral irradiance.

the computed values of spectral irradiance were uncertain by an indefinite amount.

Attention was given next to lamps being made commercially. The General Electric (GE) Model 6.6A/T4Q/1CL-200-W quartz-iodine lamp (see Fig. 1) was examined and found to have acceptable characteristics for use as a standard. It is of robust construction, in a small quartz envelope of relatively good optical quality so that the intensity usually varies but little over a considerable solid angle centered normal to the axis of the lamp. The filament is a compact coiled coil with over-all dimensions approximating 3 mm × 13 mm. The small size of the lamp envelope (about 13 mm × 5 cm) together with the small area of the filament permits placing the lamp within a few centimeters of the slit of a spectrometer. Since this lamp is being set up as a standard of spectral irradiance to be employed without auxiliary optics, relatively high irradiance at a slit can be realized simply by placing the source close to it.

Because of its high operating temperature, the quartz-iodine lamp emits a relatively large percentage of ultraviolet radiation. The high temperature is made possible through the unique chemical action of the iodine vapor[19,20] which results in the return of evaporated tungsten from the bulb to the lamp filament, thereby keeping the envelope clean and prolonging the useful life of the lamp. The design life of this lamp when operated at 6.6 A is 500 h. For calibration as a standard, the current is set at 6.50 A which usually gives a color temperature between 3000 and 3100°K, corresponding to a filament temperature around 3000°K.

The establishment of the new standard of spectral irradiance was accomplished by comparing a group of quartz-iodine lamps with three other types of NBS standards, each of which is based upon the spectral radiance of a blackbody computed from Planck's radiation equation, wherein the radiation constants $c_1 = 1.9088 \times 10^{-12}$ W cm²/ster and $c_2 = 1.4380$ cm°K.

The group of quartz-iodine lamps was first compared spectroradiometrically with the NBS standards of spectral radiance.[18] The optical arrangement is shown in Fig. 2. Additional details may be found in the reference cited. To cover the complete spectrum from 0.25 to 2.6 μ, three detectors were employed. An RCA type 1P-28 multiplier phototube was used to cover the range from 0.25 to 0.75 μ. For the range of 0.35 to 1.2 μ, an RCA type 7102 multiplier phototube was employed, while an Eastman PbS cell was used through the range of 0.5 to 2.6 μ. To eliminate the effect of spectral reflectance of the two aluminized mirrors employed with the ribbon-filament standards of spectral radiance, two plane mirrors having identically prepared surfaces were used with the quartz-iodine lamps. Actually, plane mirror M_1 was common to both optical systems (see Fig. 2). By this procedure, all instrumental characteristics were identical or closely similar for the two types of lamps. Hence, the optical and electronic factors should cancel out in the procedure. However, it was found that the light beam from the quartz-iodine lamp passed through the spectroradiometer somewhat differently and irradiated a slightly different area of the detector from that irradiated by the ribbon-filament standard. The beam of flux from the ribbon filament converged on entering the spectrometer, then diverged filling an appreciable part of the instrumental aperture, and finally at the exit slit emerged as a divergent beam. The flux from the quartz-iodine lamp passed through the spectrometer and emerged as

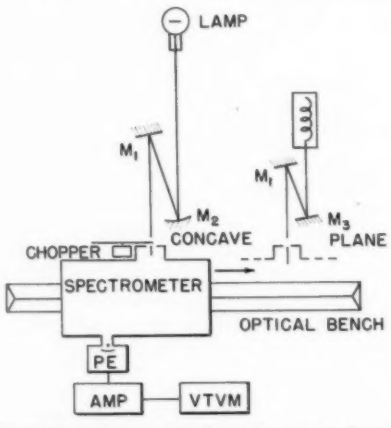

Fig. 2. Optical arrangement of spectrometer, lamp, mirrors, and associated equipment for comparing the quartz-iodine lamp standards of spectral irradiance with the ribbon-filament standards of spectral radiance.

Table I. Spectral Irradiance of Three 200-W Quartz-Iodine Tungsten-Filament Lamps[a]

Wavelength (nm)	Lamp QL-2	Lamp QL-5	Lamp QL-10
250	0.0051	0.0052	0.0051
260	0.0093	0.0093	0.0090
270	0.0158	0.0159	0.0155
280	0.0253	0.0252	0.0244
290	0.0380	0.0380	0.0369
300	0.0545	0.0548	0.0532
320	0.104	0.105	0.102
350	0.237	0.242	0.234
370	0.366	0.374	0.363
400	0.643	0.647	0.630
450	1.26	1.26	1.23
500	2.04	2.04	2.02
550	2.93	2.96	2.91
600	3.88	3.94	3.88
650	4.79	4.91	4.80
700	5.54	5.72	5.58
750	6.11	6.32	6.14
800	6.51	6.69	6.49
900	6.72	6.94	6.71
1000	6.51	6.73	6.53
1100	6.07	6.25	6.11
1200	5.53	5.67	5.55
1300	4.97	5.09	4.98
1400	4.44	4.52	4.44
1500	3.93	4.00	3.93
1600	3.46	3.51	3.45
1700	3.03	3.06	3.01
1800	2.63	2.65	2.61
1900	2.29	2.28	2.26
2000	1.98	1.97	1.95
2100	1.73	1.71	1.70
2200	1.52	1.51	1.50
2300	1.36	1.34	1.33
2400	1.22	1.21	1.21
2500	1.12	1.10	1.11
2600	1.04	1.03	1.04

[a] In μW per cm^2 per nm at a distance of 43 cm (measured from the axis of the lamp filament and normal to the plane of the lamp press) when operated at 6.50 A.

an essentially narrow "pencil" of flux, thereby being confined to a small part of the instrumental aperture and falling upon a small area of the detector. As a result, differential transmission within the spectrometer and variations in the sensitivity of the detector over its surface area* resulted in small errors of unknown magnitude. Hence, the resulting spectral energy curves for the quartz-iodine lamps, obtained by this method, require adjustment.

Three methods for determining the correction for the observed data were pursued. They are:

(a) Direct comparison, without the use of a spectrometer, of the quartz-iodine lamps with the ribbon-filament lamps by a thermopile and filter method, wherein selected spectral regions were compared radiometrically. This comparison was accomplished by focusing an image of the ribbon filament on the receiver of the thermopile by means of the two aluminum mirrors usually employed with the standard of spectral radiance. The quartz-iodine lamp directly irradiated the thermopile receiver. Correction was made for the spectral reflectance of the two aluminum mirrors. The ratio between the two radiometric readings gave a measure of the relative spectral intensities of the two sources for the different spectral regions defined by the filters employed.

(b) Measurement of luminous intensity as compared to calculated luminous intensity based upon the spectroradiometrically determined curve and the spectral luminous efficacy of the CIE standard observer. This method gave an independent evaluation of the spectral irradiance of the quartz-iodine lamps in the visible spectrum based upon NBS standards of luminous intensity, which had been assigned values by measurements relative to a blackbody at the freezing point of platinum.[21]

(c) Measurement of irradiances over selected spectral regions by employing optical filters and a thermopile found by comparison with a cavity detector to have a relatively flat spectral response and calibrated through the use of the NBS carbon-filament standard of total radiation. This method afforded an independent evaluation of the spectral irradiance from the quartz-iodine lamps based upon the NBS standard of total irradiance and the blackbodies used in its establishment.[1,2] Corrections ranging from 4.2 to 5.3% and nonselective with wavelength were indicated by the three methods. The original spectroradiometric data were accordingly corrected by 5.0%.

III. Results

Spectral irradiance data obtained on three quartz-iodine lamps are given in Table I in μW/cm^2 at a distance of 43 cm (measured from the axis of the lamp filament and normal to the plane of the lamp press) for a wavelength interval of 1 nm. It is estimated that the maximum uncertainty in the results ranges from about 8% at the shortest wavelengths in the ultraviolet to about 3% in the visible and infrared. The data have been corrected for the water-vapor absorption occurring at or near 1.1, 1.4, 1.9, and 2.6 μ. No significant radiant-energy absorption occurs at other wavelengths because of other gases normally present in the usual laboratory environment.

The quartz-iodine lamps may be employed at any convenient distance by computing or otherwise determining the irradiance at the new distance. The inverse square law should not be applied to these lamps

* Much of the variation of the detector sensitivity was eliminated by placing in front of it a quartz plate finely ground on both faces.

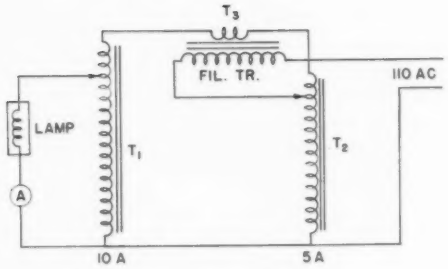

Fig. 3. Electrical circuit for lamp operation to provide smooth current control.

for distances shorter than about 40 cm. In most laboratory atmospheres the correction for water-vapor absorption will be small for distances of less than 50 cm. However, for greater distances and under conditions of high humidity, a correction may be required.[22–26] The relationship between the apparent absorption of water vapor (as indicated in a prism spectrum) and the amount of vapor is not a simple one, since each absorption band really consists of many fine lines of unequal intensity and irregular spacing. Furthermore, the attenuation at any wavelength due to water vapor is a complicated function of the pressure, temperature, and concentration of the vapor per unit volume.

Aging tests conducted on three quartz-iodine lamps indicate after 100 h of operation an increase at 6.50 A of less than 1% in total irradiance, luminous intensity, and ultraviolet irradiance around 360 nm.

IV. Use of the Standard of Spectral Irradiance

Each quartz-iodine standard is marked with an identifying number at one end of the lamp. The lamp is mounted in a metal support and is calibrated with this marked end down and with the plane of the front surface of the lower press seal set to contain the horizontal perpendicular to the line connecting the lamp filament axis and detector or spectrometer slit. The lamp tip seal is positioned away from the detector or slit. Precise setting of the lamp as regards to verticality and to rotation about the filament as an axis are important, since a few degrees displacement may result in an error of 1% or more.

The current is set at 6.50 A ac, and the lamp is allowed to operate for at least 5 min before data are recorded. Any convenient method may be employed to control the current; however, the circuit illustrated in Fig. 3 has been found very useful in this laboratory. It consists of two variable autotransformers (10-A and 5-A capacities) and a radio filament transformer. (One-half of a center-tapped 5- or 6.3-V secondary has been found to be satisfactory for smooth current control.) If a 30-V step-down transformer is available, it may profitably be used between the variable autotransformer, T-1, and the lamp.

V. Conclusions

The quartz-iodine lamp is a useful working standard for use in spectral irradiance measurements within the region of 0.25 to 2.6 μ. The methods of calibration are based upon indirect comparisons with the radiances of blackbodies and thus do not involve evaluation of filament temperature or tungsten emissivity. The principal uncertainties in the results are due to difficulties involved in accurate blackbody high-temperature evaluation and precise current settings for the various lamps. The maximum uncertainty in the results is estimated to range from about 8% at the shortest wavelengths in the ultraviolet to about 3% in the visible and infrared.

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Interferometric Measurement of Wavelengths of Infrared Atomic Emission Lines in the Extraphotographic Region

Curtis J. Humphreys

A considerable extension of the international system of wavelength standards has been achieved by direct interferometric intercomparison of accepted standards with selected infrared lines in the region beyond the limit of photographic response. A radiometric system employed successfully for this purpose scans the pattern of Fabry–Perot fringes projected upon the slit of a spectrometer. By tilting the interferometer in uniform angular motion about a vertical axis, a diametral section of the fringe system moves across the slit, generating a set of maxima that are registered on a uniformly moving record chart with the same distribution as that of the fringe diameters. Items discussed include achromatic projection, vacuum techniques, and procedures for the reduction of data.

I. Introduction

Following the invention of the parallel-plate interferometer by Fabry and Perot shortly after the beginning of the present century, a new system of spectroscopic wavelength standards, known as the "*international system*", was inaugurated. The new system, based on interferometric intercomparison of the wavelengths of appropriate lines with accepted standards, superseded the older Rowland system which had depended on the principle of superposition of grating orders. The standards that represented the starting point of the international system were lines in the visible spectrum of cadmium that had been used by Michelson to define the length of the standard meter. A fairly detailed account of the establishment and development of the international system of standards has been given by the author[1] in an article prepared for the new edition of the *Encyclopaedic Dictionary of Physics*. Briefly, the authority for control of the system of standards including establishment, maintenance, and expansion was assumed by the International Union for Cooperation in Solar Research under the leadership of George Ellery Hale. This organization held its first meeting at Meudon in 1907, which year marks the beginning of the international system. Suspended during World War I, the Union was reorganized as the International Astronomical Union (I.A.U.) and resumed meetings in 1922. Since that date, except for an interruption during World War II, triennial meetings have been held. The I.A.U., among its several commissions, includes one generally known as Commission 14, but which carries the official title: "Commission des étalons de longueur d'onde et des tables des spectres". At the 1961 Berkeley, California, meeting a new name was proposed: "Commission des données spectroscopiques fondamentales". This commission considers new wavelength material and, when such action is indicated, recommends new standards for adoption by the I.A.U. A complete record of these proceedings is published in *Transactions of the International Astronomical Union*, which appears as a triennial volume covering each meeting. These volumes constitute the most authoritative and complete tables of available wavelength standards covering, until very recently, the range between approximately 2000 and 10,000 Å. Probably the principal motivation to opening up the extraphotographic infrared region to inferometric observation lay in the fact that, during the first half-century of existence of the I.A.U. or its parent body, not a single wavelength measured interferometrically by a radiometric procedure had been submitted for consideration.

Beginning in 1955,[2] an experimental program of direct interferometric intercomparison of wavelengths by a radiometric scanning method was inaugurated at the U.S. Naval Ordnance Laboratory, Corona. This program, which has been active during essentially all of the intervening period, is described in the following section. By action at its meeting in 1958,[3] the I.A.U. accepted the results of some of the measurements under this program as the basis for an extension of the system of

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wavelength standards into the infrared region beyond 1 μ. By the time of the following meeting in 1961,[4] independent determinations by other observing teams in other laboratories, using different methods, had confirmed the 1958 submission to the extent that the coverage was duplicated, thereby satisfying long-established criteria of independence and concordance for adoption of standards by the I.A.U.

II. The Tilting Interferometer

The radiometric scanning procedure selected and devised by the author was suggested by the photographic technique in current use. The photographic intercomparison of wavelengths is carried out by simultaneous registration of the interference patterns of the selected lines obtained by crossing a Fabry–Perot interferometer with a suitable spectrograph, and by subsequent measurement and reduction of the patterns leading to an exact evaluation of the retardation. On the photographic plate the usual lines are replaced by vertical arrays of short horizontal arcs having the same appearance as a circular fringe pattern in monochromatic light masked by a vertical slot symmetrically placed along a diameter. Interference spectrograms have been reproduced in numerous reference texts as, for instance, those by Candler,[5] Harrison *et al.*,[6] and White.[7] For purposes of reduction, the positions of the images in the arrays are measured, and the reduction program is based on the evaluation of ring diameters appropriate to successive orders. The theory of the Fabry–Perot interferometer and procedures for data reduction, discussed first by Fabry and Buisson,[8] have been treated by many authors including Meissner,[9] Williams,[10] and Candler.[5] A brief discussion was included in a paper by Humphreys.[11] Specialized topics have been emphasized in various short articles. Meggers[12] discussed the method of exact fractions for the unambiguous determination of the retardation. Calculation of fractional orders from measurement of the ring diameters only, thereby eliminating the requirement of precise knowledge of the geometry of the optical system, was treated independently by Childs[13] and by Burns and Kiess.[14] Least-squares treatments of the ring diameters to achieve proper weighting have been developed by Roeser[15] and by Rolt and Barrell.[16]

Progress in the development of the radiometric scanning system for observation of patterns of infrared lines, together with any new wavelength material made available by the program, is reported in the series of reports covering the Foundational Research Program at the U.S. Naval Ordnance Laboratory, Corona, California.[17] Several brief preliminary papers have been included in programs of the Optical Society of America.[18] Open literature publications include the presentation by Humphreys and Paul[19] at the International Colloquium on Interference Spectroscopy at Bellevue, 1957, and the paper by Humphreys[20] at the Xth Colloquium Spectroscopicum Internationale, University of Maryland, 1962. The method was also described at a Navy Science Symposium sponsored by the Office of Naval Research in 1957.[21]

The unique advantage of unambiguous determination of retardations associated with the observation of complete Fabry–Perot fringe patterns was the consideration that weighed most heavily in the adoption of the described method of radiometric scanning of interference patterns. Since obviously only one pattern could be scanned at one time, the photographic technique of simultaneous registration could not be employed. The best substitute appeared to be use of a sequential scan in which observations of standard lines and experimental lines were alternated. This procedure involves the obvious assumption that any variation in the retardation between successive observation of standard patterns proceeds at a uniform rate. Because of the somewhat limited circulation of the NOL-Corona report series, some of the previously published[17] details are repeated, including modifications of the technique or improvements.

The essential features of the interferometer and accessories, in an arrangement employed previous to recent modifications, are displayed in a photograph reproduced as Fig. 1. Essential items shown include exciter unit with directional antenna, electrodeless source, interferometer in fixed etalon mount, lenses for collimation and fringe projection, and motor with linkage for moving the interferometer. The interferometer is set up in front of the slit of a high-resolution spectrometer described in an earlier issue.[22] This instrument, outside the reproduced picture, serves as the monochromator to permit selection of the line under study. It is hand set to the appropriate wavelength, and the setting is optimized for maximum deflection. With the setup shown it is necessary to refocus the projecting lens according to

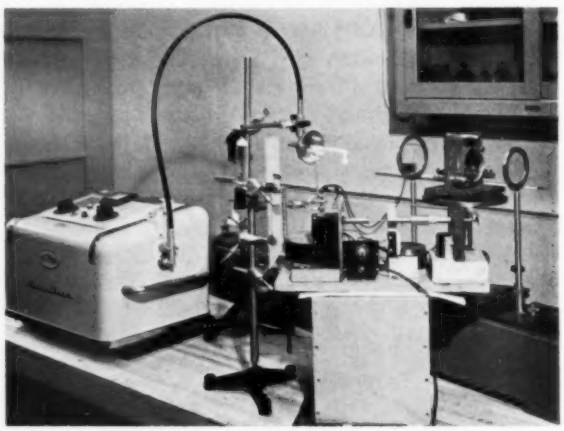

Fig. 1. Early form of interferometer and accessories.

Fig. 2. Presently used interferometer system showing vacuum housing and reflecting optics.

the wavelength region under observation, since an achromatic lens is not available for the range of wavelengths covered by the experiments. The rotation or, as some prefer to call it, tilting of the interferometer is accomplished by a tangent motion actuated by a synchronous motor that turns a micrometer screw through reducing gears. Since it is desirable to realize uniform angular rotation, the motion during one duty cycle should not exceed the angular displacement on either side of the optic axis within which the angle does not depart from its tangent by more than the random errors. This is kept within about 5° on either side of the setting corresponding to the center of the fringe system, or within a total angular displacement of about 10°. A reversing circuit is used so that scanning may be accomplished in either sense, and, in general, an equal number of scans in both directions are made and included in the measurements.

The operating features of the setup have been retained, in principle, throughout the period of the experiments. The two most important modifications have been the enclosure of the interferometer in a vacuum chamber and the substitution of mirrors for all lenses in the system. These modifications are illustrated in Fig. 2. The evacuated enclosure consists of a substantial circular plate resting on the turntable and serving as a base for the interferometer; a metal bell jar with opposed windows in side arms rests on the plate with an O-ring seal. Evacuation is provided through a connection at the center of the top of the bell jar. A short length of pressure hose provides sufficient flexibility to permit the small amount of angular motion. Among the advantages of evacuation are: avoidance of the correction for dispersion of the air which is subject to some uncertainty even with a reasonable degree of control of temperature and readings of pressure and humidity, and increased stability of the interferometer adjustment with almost complete absence of transient fluctuations in the length of the interference path. Observation of wavelengths in vacuum also permits direct calculation of wavenumbers as reciprocals.

The substitution of mirror optics is accomplished by use of two off-axis paraboloidal mirrors. The mirror used for ring projection is an element of 1-m focal length, 15 cm in diam, and designed 10° off-axis. It is used in a folded system in a vertical plane together with a small plane mirror in the path of the converging beam. The principal advantage of this system is complete achromatism permitting a fixed setting. Another advantage is freedom from absorption by lens material. Glass or quartz lenses cannot be used successfully beyond the water absorption at 2.7 μ. To realize the full advantages of the system it will be necessary to replace both the interferometer plates and the windows of the bell jar with fluorite. The necessary elements are now under construction. Optimum definition of the image formed by a parabola requires a precise satisfaction of the optical conditions, namely, rays emanating from the focal point and reflected as a parallel beam or, as in this arrangement, the reverse situation with projection at a point. The requirement for stopping down the slit with a narrow horizontal slot is explained in a following section. The actual scanning aperture approximates a pinhole opening closely enough that with careful adjustment projection of fringes with optimum definition is obtained. For illuminating the interferometer with collimated light from the source a stock-item Perkin–Elmer parabola is used in a horizontal folded arrangement. The illustration shows the disposition of two sources, one aimed directly at the mirror, the other brought into active use by elevating a plane mirror into the optical path by a rack and pinion. It is thus possible to switch rapidly from an experimental source to a source of standard wavelengths, each being powered by its own exciter unit. Use of the mirror for illumination results in more efficient energy utilization than use of a lens. Only one reflecting surface is involved, and there is no absorption loss.

In considering the methods of producing a translation of the fringes across the entrance slit of the spectrometer two possibilities suggest themselves. The one actually selected is the rotation of the interferometer element; the other possibility would be to rotate the plane mirror in the projection system. The choice is based on the fact that at the slit there is a superposition of the interference pattern upon the projected image of the source. If the plane mirror is rotated, the source image and interference pattern behave as if rigidly attached together so that, if the center of the pattern coincides with maximum illumination, both move off the slit together, resulting in rapid attenuation as the fringes of increasing radius cross the slit. If, as in the system in use, the interferometer element rotates, the maximum illumination remains on the slit and the successive orders in

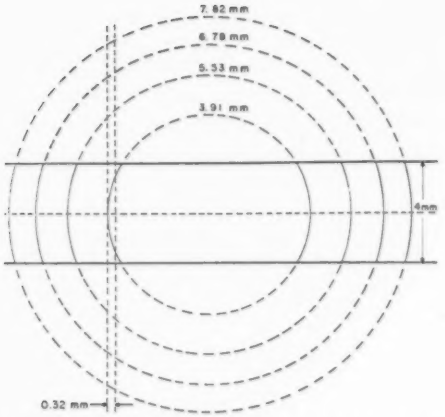

Fig. 3. Configuration of fringe arc in slit opening at point of maximum deflection, for typical setting of slit and horizontal diaphragm.

passing pick up this illumination. This is precisely the technique used in the operation of a Michelson echelon as described in all standard texts on optics. It is recalled that with the echelon at most only two orders are visible at one time with significant intensity. This discussion is introduced in answer to criticism that has been offered on several occasions that the method is impractical because of energy attenuation for orders away from the center of the pattern.

The operation of the scan is illustrated by Fig. 3, which represents an interference pattern idealized to show the fringes as geometric circles in monochromatic light projected upon the slit jaw faces. Actually, a composite projection of the patterns of all wavelengths appears here to be sorted out by the spectrometer. This composite of patterns moves to the right or left across the slit as the interferometer rotates. A diaphragm with a horizontal aperture limits the portion of the circular pattern actually scanned to a relatively narrow diametral zone. This limitation of the vertical length of the scanning aperture, a section of the spectrometer slit, permits realization of several objectives which will be explained. The figure, drawn to scale with a magnification factor of 10, for a wavelength 0.85 μ, focal length of the projecting system 600 mm, interferometer separation 20 mm, rings erupted to the positions of integral orders without fractional residue, with other pertinent dimensions indicated, serves to illustrate some of the experimental problems and possible sources of error associated with the method. These parameters are typical of the experimental conditions and location of standards for the early period of the program.

A criticism of the method, based on what appear to be valid considerations, is that a source of error may be the use of a finite scanning aperture as required by energy considerations. It is believed that this error has been reduced below the level of significance. A brief qualitative discussion is introduced, however, to explain the aperture effect and to indicate measures taken to reduce it. The portion of the slit used as the scanning aperture is a vertical rectangle. If the assumption is made that the fringes are geometric circles, that is, infinitely narrow, the maximum energy would be transmitted under the condition shown in the figure when a chord of the circle is inscribed in the aperture. If we call the diameter of the circle D, and the width of the slit d, the distance traversed in the scan from a maximum to the maximum symmetrically placed on the opposite side of the center is $D - d$. According to the reduction scheme already mentioned,[13,14] the fractional part of the order of interference is given by

$$f = \frac{D_n^2}{(D_{n^2+1} - D_n^2)} - (n - 1),$$

where n is an integer. If, instead of measuring the true ring diameter, one measures $D - d$, the apparent value of the fraction becomes

$$f = \frac{(D - d)_{n^2}}{(D - d)_{n+1}{}^2 - (D - d)_{n^2}} - (n - 1).$$

The effect of the error in the measurement of the ring diameters on the fractional part of the order, assuming the indicated geometry, can be calculated in specific instances if the wavelength, the plate separation, the width, and the focal length of the projecting lens are known. It turns out that the apparent fraction is less than the correct fraction by a calculable amount. If the wavelengths of the experimental line and of the comparison standard are nearly equal, the respective fractional orders will be equally affected in the reduction, and the derived wavelength will come out exactly the same as if there had been no error in the measured diameter. This condition can seldom be realized in practice, since, in general, the standards are of lesser wavelength than the experimental lines. If we assume geometric circle fringe form and inscribe the chord in the aperture for maximum energy, the error in the wavelength determination may amount to a few thousandths Å where lines near 1.5 μ are compared with standards near 0.9 μ. This would, of course, be unacceptable if uncompensated. The compensation for the aperture error is achieved experimentally by making the aperture as small as possible in both dimensions. A reduction of either dimension will shorten the arc of the inscribed fringe. Under improved experimental conditions the width of the horizontal slot is reduced to about 2 mm. Under that condition the arcs of all observed fringes will be cropped, so that they approximate a straight line form, the approximation improving as the diameters increase. In actual practice the aperture error has not been experimentally detectable, when horizontal slots of different widths have been tried out.

The use of the horizontal slot serves two other purposes. If it were not used at all, sections of fringes of several orders would appear in the slit at one time. This would not only introduce an error of setting on the innermost fringe affected but also introduce unwanted optical noise marring the resolution and definition. The reduction of the aperture to approximate a pinpoint opening also permits realization of the optimum conditions for use of a paraboloidal mirror for projection of fringes as already discussed. Figure 4 is a reproduction of a record made under optimum conditions realizable with a strong line. It displays a pattern of more than 100 fringes originating in λ 13,504 Å, Ar I, with a 30-mm separator, a horizontal aperture of 2 mm, and a slit 0.15 mm wide. The limitation on the number of orders observable is set by the ratio of the actual slit-width to the separation of fringes as projected.

III. Measurement and Reduction of Records

The records are processed in a manner to facilitate use of a computer program for a part of the reduction procedure. The settings of fringe positions are registered on punch cards with the aid of a semiautomatic reading machine. These cards provide the starting data for a program based on a least squares formula devised by Rolt and Barrell[16] to give the appropriate weighting to ring diameters according to position. The general form of this formula as quoted by Candler,[5] p. 217, is:

$$\epsilon = \frac{\sigma\Sigma - sS}{pS - s\Sigma},$$

where

$$\Sigma = d_1^2 + d_2^2 + \ldots + d_p^2.$$
$$S = d_2^2 + 2d_3^2 + \ldots + (p-1)d_p^2.$$
$$s = 1 + 2 + \ldots + (p-1).$$
$$\sigma = 1^2 + 2^2 + \ldots + (p-1)^2.$$

For the case of four rings it assumes the form:

$$\epsilon = \frac{7D_0^2 + 4d_1^2 + D_2^2 - 2D_3^2}{-3D_0^2 - D_1^2 + D_2^2 + 3D_3^2}.$$

It is the practice of the authors to make use of four rings only, beginning with the innermost that is fully erupted. The output of the computer is a tabulation of the fractional part of the orders. The calculation of whole orders by the method of exact fractions is carried out manually. Even with the greatest care an occasional order ambiguity will appear. Such ambiguities can be eliminated by repeating the observations with two or more etalons having lengths not related by simple integers. The correction for dispersion of phase change at reflection is made where indicated by a method described by Meggers[23] involving use of a large and a small separation of plates. The procedure is an algebraic one to eliminate the apparent partial penetration of the film at reflection.

IV. Special Equipment Items

Most of the components used in these experiments are fairly conventional. The interferometer plates are of unusually large diameter to provide sufficient aperture to compensate for relatively low infrared energy. For nearly all reported experiments a selection has been made from three pairs of plates, 80 mm in diameter. Two pairs are of Corning optical quality vitreous silica; the third is a pair of matched quartz plates transmitting along the optic axis and with respective optical rotations in the opposite sense. In general, very light evaporated aluminum coatings have been used, it being considered preferable to observe a fairly large number of patterns than a small number permitted by denser coatings that would be characterized by optimum resolution but available for only the most intense lines. The most practical coating appeared to give about 30% transmission for each plate or approximately 10% for the combination. Although probably the most satisfactory material for the 1- to 2-μ region, aluminum exhibits two deficiencies: opacity increasing to the point that it is not practically useful beyond 2 μ, and a discontinuity in optical properties between 0.8 and 1.0 μ. The behavior of aluminum films in that region, reported by Bennett *et al.*[24] and by Kleiman,[25] makes it difficult to span the noted interval in wavelength intercomparisons because of uncertainty in the evaluation of the correction for dispersion of phase change at reflection. This anomaly led to an error in early measurements where standards were chosen near 0.85 μ. Later experiments have utilized standards of wavelength near

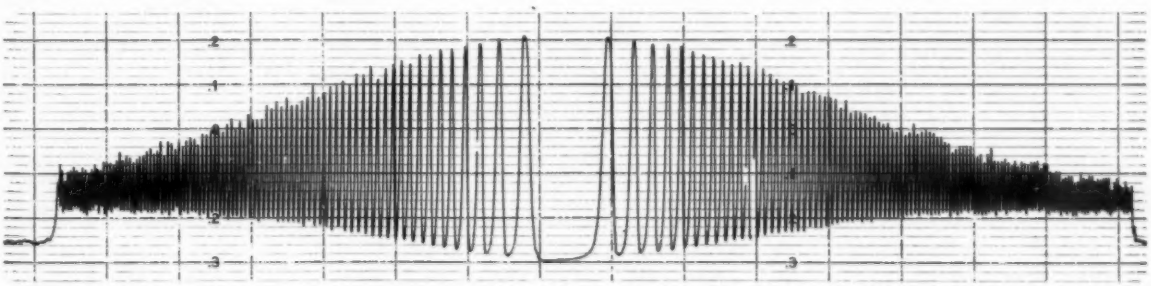

Fig. 4. Pattern of Ar λ 13504, 33-mm etalon, minimum scanning aperture.

1 μ or greater. A limited number of exploratory experiments has demonstrated the feasibility of using germanium coatings for the 3- to 4-μ region.

The mountings for the fixed etalons may be described as an enlarged version of the design first employed by Fabry. The features of this design are obvious from a study of Fig. 1. Modifications in minor details are described in the NAVORD/NAVWEPS Report series.[17]

The etalons or spacers actually or in principle make use of three pins of equal length mounted in the periphery of a circle 120° apart. For separators up to 30 mm, invar pins have been fitted into a metal ring. Testing for parallelism by visual observation of the assembled interferometer illuminated with a noble-gas or mercury source is employed in the final honing. The largest separators actually used in the accumulation of published results, namely 45 mm and 63 mm, were fabricated of satin-finish silica tubing. The three-point contact arrangement was produced by building up fused silica beads 120° apart on the sawed ends in opposed fashion to line up the extremities in contact with the reflecting surfaces.

Microwave-excited electrodeless discharges have been used in all recent work both for exciting the element under study and as sources of standard lines. Certain specialized designs are described by the author[22] in a recent issue of this journal. For proposed work use of the Engelhard source,[26] a type of Geissler discharge developed for excitation of the primary standard of length, the Kr^{86} line of wavelength in vacuum, 6057.80210 Å, is contemplated. A specially designed cryostat maintaining the temperature of the triple point of nitrogen is required for operation. The gaseous laser, as developed by Javan *et al.*,[27] offers considerable promise owing to simultaneous realization of high intensity and great coherence length. It has not been used in this program to date. There is still some question of operational stability and consequently of reproducibility of wavelengths.

Lines of Ar I, in the category described in the Paschen notation as $1s - 2p$, have been used almost exclusively as standards for intercomparison in these experiments. The values used for this group of lines lying between 6677 A and 11,488 Å were adopted by the I.A.U. at the

Table I. Partial Array of Ar I Level Combinations Indicating Precision of 1959 Wavelengths

		$2s_5$	$3d_3$	$3d_1'$	$3s_1''''$	$3s_1''$	$3s_1'''$
		$j = 2$	2	3	2	2	3
	NOLC 1959 →	20324.713	18995.164	20572.795	21497.232	21661.375	21678.179
	I.A.U. 1955 values						
			10673.566	12439.321			
$2p_{10}$ $j = 1$	10958.339		9366.374	8036.825			
	1360.661		1360.661				
			12487.663		12112.325			10681.772
$2p_9$ $j = 3$	12319.000		8005.713		8253.794			9359.179
	154.510				154.510			
	2135.453				12343.393	11078.867		
$2p_8$ $j = 2$	12473.510			2135.453	8099.284	9023.723		
	469.990							
$2p_7$ $j = 1$	12943.500				620.281			
	620.282			16940.583	13367.111		11668.709	
$2p_6$ $j = 2$	13093.792	1826.940		5901.372	7479.003	1514.440	8567.583	1826.940
	1514.439							
$2p_5$ $j = 0$	13910.512							
						13313.209		
$2p_4$ $j = 1$	13987.949					7509.283	1258.865	
	1258.865							
								13272.636
$2p_3$ $j = 2$	14145.940							7532.239
							13678.550	
$2p_2$ $j = 1$	14352.657						7308.718	
$2p_1$ $j = 0$	15578.859							

Table II. Observed Vacuum Wavelengths of ArI Lines in the Infrared

λ_{vac} (A)	Humphreys and Paul[29]	Littlefield and Rowley[21]	Peck *et al.*[20]
8266			0.794_5
9125			0.471_4
9227			0.0302
10472			0.922
10676	0.489		0.4907
10684	0.698		
11081	0.901		
11671	0.903		
12115	0.639		
12346	0.770		
12406	0.220	0.218	
12442	0.724		
12459	0.523		
12491	0.079	0.079	
12705	0.755		
12806	0.241	0.247	0.2401
12960	0.203	0.203	0.2004
13011	0.822	0.821	
13217	0.606		
13231	0.727		
13276	0.266	0.266	
13316	0.850	0.855	
13370	0.766	0.768	
13507	0.883	0.882	0.884
13626	0.383	0.391	0.387
13682	0.290	0.292	
13722	0.327	0.329	0.3271
14097			0.4914
16945	0.210	0.213	0.209

1955 meeting.[28] Both on account of the discontinuity in the properties of aluminum and because it is advantageous to shorten the wavelength span between experimental patterns and standards, a selection was made among the seven $1s - 2p$ lines included between λ 9122 Å and λ 11,488 Å. Under the conditions of these experiments where sources must be operated to achieve high output, the coherence length of path for wavelengths much below 0.9 μ is not sufficient to permit use of etalons up to 63 mm in length. In some instances the Hg^{198} line, λ 10,139 Å, has been used as a standard. The operating conditions for a mercury source must be controlled much more carefully than for a noble gas. Furthermore the population of usable lines in the infrared near or beyond 1 μ is small. Source tubes are operated with as little loading as practicable to minimize overheating. No temperature control has been employed other than maintenance of uniform ambient temperature provided by the air conditioning. The ambient temperature has been maintained near 19°C. When using uncooled lead sulfide cells, responsivity is significantly improved by holding the ambient temperature at the lowest practical level. A description of the detecting, amplifying, and recording equipment has been included in the earlier paper already mentioned[22] and will not be repeated here. The essential features of the system are: a selected lead sulfide cell, a narrow band-pass amplifier designed by Wilson, and any one of a number of commercially available recorders, preferably a recorder having a galvanometer mechanism and linkage to give deflections at right angles with direction of chart movement.

V. Discussion of Results

To be useful as a standard wavelength in the analysis of complex spectra the result of an interferometric determination should represent in wavenumbers an absolute accuracy of about ± 0.001 cm^{-1}. In the visible region this requires wavelength determinations to be made ideally to about one part in 10^8. Because of the reciprocal relation the requirements are eased very rapidly as one proceeds toward the infrared. This may be illustrated by the following tabulation prepared in part by Littlefield,[4] showing the wavelength precision equivalent to 0.001 cm^{-1}:

λ (Å)	Δλ corresponding to $\Delta\sigma = 0.001$ cm^{-1}
40,000	0.016
20,000	0.004
10,000	0.001
5,000	0.00025
2,000	0.00004
1,000	0.00001

It is thus apparent that an arbitrary precision to categorize a class of standards as to quality is rather meaningless unless the region is specified. It is also apparent that in terms of wavenumber precision there is a considerable experimental advantage associated with the determination of standards for the infrared region, as compared with the visible to ultraviolet.

In spite of the fact that any mechanical scanning method—particularly one involving two moving systems, interferometer and recorder—cannot match the precision obtainable by photography on a substantially mounted stationary plate, the author is confident that with all satisfactory patterns an absolute accuracy of one part in 10^7 has been achieved for observations in the 1- to 2-μ region. No figure beyond the thousandth place in angstroms has been retained in published results. Evidence of the absolute accuracy of the wavelength values is presented in the form of a quadratic array demonstrating how closely the Ritz combination principle is satisfied for part of the $2p - 2s$, and $2p - 3d$ transitions in Ar I. The material, displayed as Table I, is selected on the basis of repeated observable level differences. Systematic errors appear rather improbable, particularly where the level differences amount to between 1000 and 2000 cm^{-1}.

Owing to fairly limited circulation of the *Transactions of the International Astronomical Union*, two tables are reproduced from the latest volume.[4] The first, Table

Table III. Infrared Standards of Ar I Based on the Combination Principle

λ_{vac} (Å)	λ_{vac} (Å)	λ_{vac} (Å)
8877.237*	13722.326*	20762.662
9197.162*	13829.497*	20816.722*
9294.078*	13911.276*	20990.015
9343.144*	13996.633*	20991.839*
9488.662*	14097.492*	21041.575*
9954.574*	14178.587*	21172.154
10256.835*	14253.089*	21338.709*
10480.904*	14581.442*	21540.086*
10676.490*	14723.568*	22045.578*
10684.697*	14743.167*	22083.206*
10686.330*	14837.535*	22118.663*
10703.915*	14978.661*	22215.794
10725.164*	15034.621*	22539.68
10776.319*	15035.281	23139.519*
10864.051*	15050.614*	23141.082
10883.921*	15056.681	23191.815
10895.344*	15175.884	23475.842
10953.725*	15176.837*	23851.548*
11081.901*	15333.533*	23973.060*
11251.430*	15357.324*	24019.782*
11396.818*	15559.709*	24027.101
11444.964*	15739.207*	24937.849
11470.684*	15780.924*	25132.125*
11649.055	15797.471*	25140.144
11671.903*	15821.097*	25346.74
11690.803*	15887.500*	25494.602*
11722.693*	15952.764	25512.189*
11899.888*	15993.858*	25668.023*
12029.938*	16127.060*	26122.899
12115.639*	16184.443*	26187.567
12143.059*	16268.513*	26550.284*
12346.767*	16296.558	26612.554
12380.579*	16524.381*	26843.036*
12406.221*	16744.652*	26917.052*
12442.724*	16864.691*	27152.861*
12459.522*	16945.212*	27293.202
12491.079*	17406.661*	27363.801*
12557.758*	17449.667*	27418.954
12625.072*	17450.012*	27760.080
12641.936*	17919.521*	27791.395
12705.755*	17919.618*	27793.527
12736.901*	18236.328*	27984.858*
12749.719*	18353.015*	28202.444*
12806.237*	18432.796*	28245.954*
12936.728*	18637.376*	28321.769*
12960.202*	18750.124*	28435.030*
13011.821*	19129.028*	28505.735*
13031.988*	19300.183*	28538.398*
13217.604*	19822.918*	28620.230*
13231.722*	19829.128	28697.871*
13234.515*	19866.367	28782.933*
13276.265*	19950.515*	28843.089*
13305.949*	19971.181*	29134.040*
13316.850*	19997.688*	29280.665*
13370.765*	20031.141*	29796.791*
13371.482	20035.563*	30462.070*
13503.097*	20074.415*	30921.192
13507.882*	20247.189	30996.228*
13547.908*	20322.555*	31333.032*
13577.324*	20574.429*	32235.344*
13603.050*	20621.855*	32256.30*
13626.382*	20652.772*	32305.909*
13682.290*	20721.991*	32333.872*

II, is an intercomparison of direct interferometric measurements of wavelengths of lines of Ar I, also in the categories $2p - 2s$ and $2p - 3d$ which comprise the most intense extraphotographic lines. The three sets of wavelengths are by Humphreys and Paul,[29] by Peck *et al.*,[30] and by Littlefield and Rowley,[31] respectively. The three sets of independent measurements by completely different methods also attest to the high degree of accuracy. Peck and his associates made use of a specially designed Michelson interferometer with an electronic fringe counter.[32] Littlefield and his associates used a reflection echelon[10] in vacuum.

An important result of the measurements on Ar I and on Ne I as well was the filling in of gaps in knowledge of the precise values of the energy levels. With the establishment of the $2s$ and $3d$ levels in these spectra on the basis of interferometric measurement, it became possible to calculate the wavelengths of a large number of lines—many of them too weak for interferometric measurement or out of range of response of detectors in use—with a precision equal to that of direct interferometric measurement. The determination of such Ritzian standards by calculation has been accepted, in principle, by the I.A.U. Table III is a set of such calculated standards comprising the transitions, $2p - 2s$, $2p - 3d$, $3d - 3p$, $2s - 3p$, and $3p - 3s$, in Ar I.

The number of precise wavelength standards for the infrared is still insufficient to provide either satisfactory spacing or adequate wavelength coverage. The heavier noble gases, krypton and xenon, provide adequate

Table III. continued

λ_{vac} (Å)	λ_{vac} (Å)	λ_{vac} (Å)
32888.638*	39835.337	55044.135
32939.617	40008.658	55606.374
33079.076*	42044.101	56039.363
33148.442*	42343.260	59348.099
33293.448*	42402.815	61257.246
35068.106	42622.276	73924.58
36220.99*	43444.978	76889.96
36312.640*	43660.972	77331.927
36492.381*	43674.073	77453.33
37013.814*	45278.146	78393.313
37143.805*	45512.47	81736.007
37186.06*	45535.495	82372.594
37261.656*	45574.89	112455.59
37921.74*	45926.608	
38331.36*	45949.400	
38640.832	46781.022	
38811.29	47151.686	
39329.852	49399.623	
39498.745	49529.443	
39804.783	53912.483	

* Observed lines; the wavelengths given are the predicted ones.

source elements, particularly if used as enriched isotopes. Littlefield[33] has already made measurements on Kr^{86} I in both the photographic and photoconductive regions employing the reflection echelon. These measurements should be repeated for confirmation by the author's method. Xe I, not very satisfactory as the spectrum of the naturally occurring isotopic mixture, owing to both isotope and hyperfine structure, appears promising when the now available isotope of mass number 136 is used. This spectrum promises to be the best available and at the same time an easily usable source of lines in the 3- to 6-μ region, which includes the strongest $2p - 3d$ transitions.

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Circulating Loop for Infrared Spectra of Reacting Gases and Other Applications

D. F. Smith, W. G. Schwab, and T. G. Burke

A circulating loop providing for the examination of the infrared spectrum of corrosive gas mixtures is described. Its uses are illustrated by the study of the xenon–fluorine reaction and by the determination of saturated vapor pressure of uranium hexafluoride at pressures below 1 cm of mercury.

A circulating loop has been constructed for use in obtaining the spectra of reaction products of such corrosive gases as fluorine. This loop has proved useful far beyond the initial expectations. It is described here, and its range of utility is illustrated by two specific examples.

A schematic diagram of the loop used in these studies is shown in Fig. 1, and photograph of a slightly different loop is given in Fig. 2. The essential parts of the loop include a piston pump actuated by external magnets, a ballast volume, an infrared cell located in the beam of a spectrophotometer, two U-tubes of 6.3-mm nickel tubing and valves to permit passing the gas through the ballast volume or bypassing the isolated ballast volume. The loop is connected with 6.3-mm copper tubing to a supply and evacuation manifold which is equipped with several kinds of pressure gauges.

The piston pump diagrammed in Fig. 3 is a modification of the double action pump described by Rosen.[1] The simplification results in a more compact single-action pump with a smaller dead volume. Normally the pump is operated at about 100 strokes per min, but the speed can be reduced to less than 25 strokes per min or increased to more than 150 strokes per min. Since the displacement is about 25 cc per stroke, the gases in the loop are quite well mixed.

The infrared cell, shown in Fig. 4, has a volume less than 30 cm^3. A tapered hole is cut through a 5.08-cm diam monel bar to give a cell 6 cm long. Silver chloride windows 2 mm thick are used. The larger 35-mm diam window is sealed by a circular flange screwed to the cell body. The smaller 25-mm diam window is sealed with a rectangular flange which fits in the spectrophotometer cell holder. Usually, teflon gaskets 12 to 25 μ thick are used to isolate the AgCl from the monel to avoid corrosion, but these may be eliminated. When working with corrosive materials, replacement of cell windows must be done rather frequently. With this design, the windows can be replaced inexpensively and quickly.

As can be seen in the photograph (Fig. 2), the U-tubes are mounted side by side so that they may be accommodated in baths in either the same or in two different dewar flasks. The volume of the primary loop, exclusive of the 687 cm^3 ballast volume, is 111 cm^3. This means that a condensable material present in the loop and ballast volume can be condensed in the U-tubes, and the ballast volume can then be isolated. On warming the U-tubes, the partial pressure of the condensable material is increased by a factor of 7.19. In many cases the pumping is more effective if a "non-condensable" gas is present to function as a carrier. Fluorine, which is transparent, usually serves this purpose well. In trapping a condensable material, the dewar with the cold bath is placed on the U-tube on the exit side of the pump and the spectrophotometer wavelength is adjusted to a strong infrared band. The flow and trapping is continued until the infrared absorption of the condensable material is negligible.

The rubbing of the piston on the cylinder wall scrapes the nickel fluoride off the wall, exposing a fresh nickel surface which then reacts with fluorine. The nickel fluoride dust so formed accumulates in the infrared cell and impairs the loop efficiency. For this reason the loop is taken apart and cleaned with warm water after every few hundred hours of operation.

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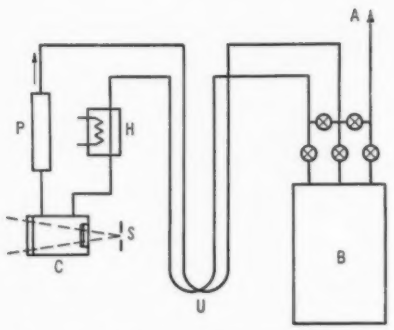

Fig. 1. Schematic diagram of loop. P—piston pump, C—infrared cell in infrared spectrophotometer beam, U—U-tubes, B—ballast volume, A—to evacuation and supply manifold.

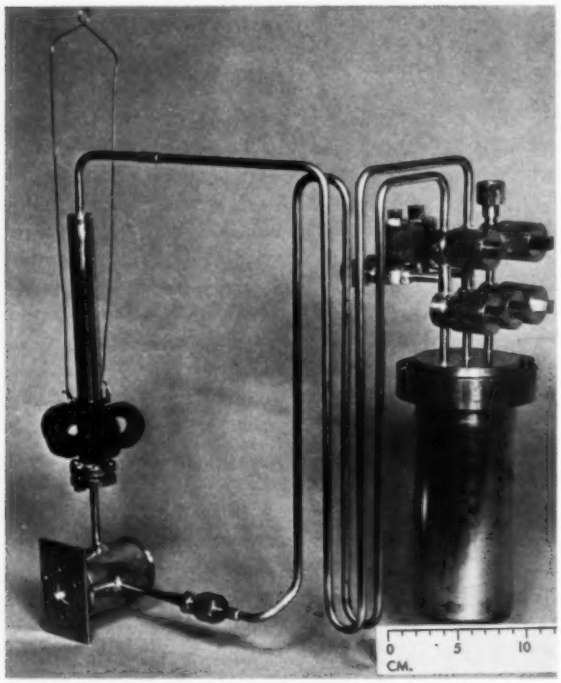

Fig. 2. Photograph of loop.

The most obvious application of the loop is the study of chemical reactions. The reaction between xenon and fluorine[2] was investigated with the loop shortly after the initial preparation of XeF_4 by Claassen *et al.*[3] was reported. Since the reaction reported by them involved heating a mixture of xenon and fluorine, a small electrical heater and a thermocouple junction were bound to the nickel tubing with fiberglass tape. Additional insulation was provided by overwrapping with alternate layers of aluminum foil and fiberglass tape. Care was taken to keep the heated zone short (about 8 cm) and the transition zone abrupt. The heated zone was located close to the infrared cell. The gas flow was from the heated zone into the infrared cell, so that the spectrum of the reaction products could be observed. A Variac was used with the heater to adjust the temperature. When a xenon–fluorine mixture was first circulated in this system, and the temperature increased, the spectrum indicated that not XeF_4, but rather another compound, later identified as XeF_2, was formed. Since the XeF_4 absorption started to increase in intensity only after the XeF_2 absorption bands had become appreciable, it was possible to prepare XeF_2 with only a low yield of XeF_4 by freezing the XeF_2 in a U-tube as it was produced. Since the Xe, F_2, and XeF_2 mixture passed through the infrared cell before going to the U-tubes, the XeF_2 absorption at 560 cm^{-1} could be taken as a measure of the XeF_2 production rate. This absorption changed when the heated zone temperature changed, so that it was easy to show that the production rate increased with increasing temperature. With different partial pressure of xenon or fluorine, the changing absorption of XeF_2 indicated that the production rate increased with increasing partial pressure of xenon or fluorine.

Some of the advantages of this loop for this kind of study can be enumerated. The identity of the reaction products formed can be established while the reaction is in progress. The rate at which a particular reaction product is formed is indicated by the rate at which

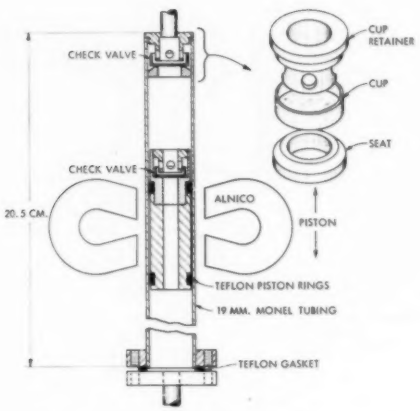

Fig. 3. Schematic diagram of pump.

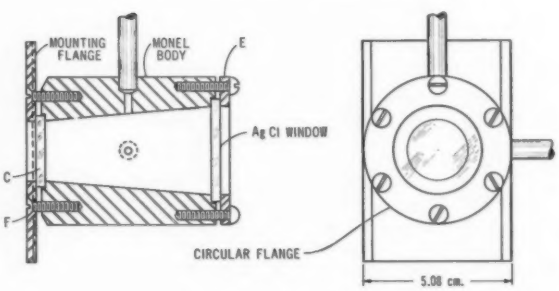

Fig. 4. Infrared cell.

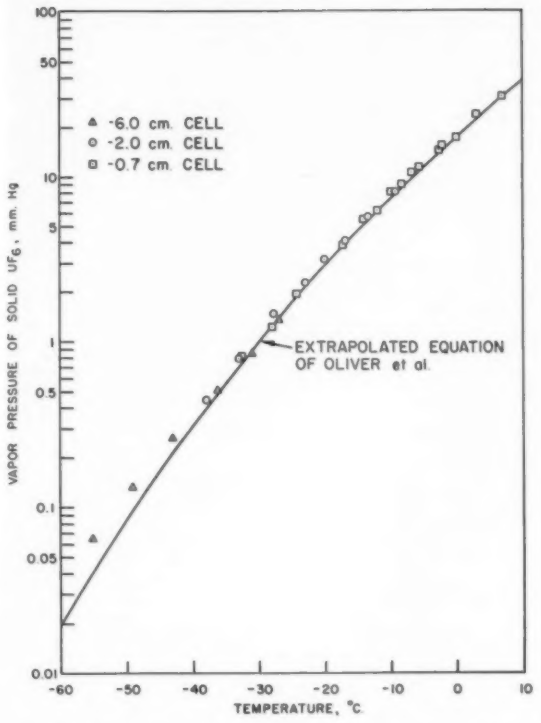

Fig. 5. Vapor pressure of UF_6 as determined with loop.

an absorption band of this product increases. The dependence of this reaction rate on such variables as reaction temperatures and partial pressures can be noted, and the conditions can be adjusted to give an optimum yield of one particular compound. Even if the infrared band has not been identified because the compound has not previously been prepared, it may be possible to prepare and purify the material responsible for the band directly in the loop, and then identify the material by other methods.

Another important application is the measurement of vapor pressures of corrosive material at pressure below 10 mm Hg. It is in this lower pressure range that small concentrations of impurities lead to biases in the vapor pressure measured by conventional methods. Thus, there are no reliable measurements of the vapor pressure of UF_6 below 0°C reported. The sublimation pressure of UF_6 has been measured with the loop in the range of 0 to −55°C. The infrared absorption of the strong 625 cm^{-1} UF_6 band was measured in cells 6 cm, 2 cm, and 0.67 cm long, with dewars containing various cold baths on the U-tubes while a mixture of UF_6 and fluorine was circulated in the loop. The absorption of the UF_6 band was calibrated by mixing the samples of known concentrations of UF_6 and fluorine in the loop, and determining the absorption with various measured sample pressures. A plot of the sublimation pressure vs temperature is given in Fig. 5 together with a plot of the vapor pressure calculated from the equation determined by Oliver *et al.*[4] from measurements in the 64–0°C range. The two examples given here serve to illustrate the adaptability of this circulating loop to a variety of applications. Other more elaborate circulating loops designed for specific purposes have been built, but these have been more cumbersome to use, and the additional complexity has actually resulted in scarcely any improvement in the performance of the simple design presented here.

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Errata

W. T. Welford, "Bubble Chamber Optics", Appl. Opt. **2,** 981 (Oct. 1963).

On p. 990, top line of right-hand column should read:
"of the kind used in aerial survey work (31, p. 4 of ref. 30)"

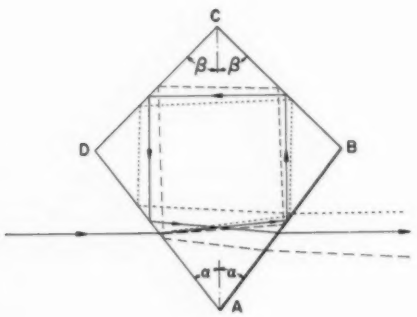
On p. 991, second line of last paragraph in first column should read:
"machines[1, 30] were the . . . ."

On p. 993, fourth paragraph of Sect. D should begin:
"A. J. Oxley (ref. 30, p. 9) . . . ."

Patents *continued from page 1116*

3,057,248 9 Oct. 1962 (Cl. 88-1)
Dispersion prism with no deviation.
B. SHERMAN. Assigned to Barnes Engineering Company. Filed 13 Apr. 1961.

A solid glass prism, resembling in shape a kite, will transmit a range of wavelengths without deviation. The angle BCD may be 90°, while the angle BAD is less than 90°. A minimum value of 1.35 for the index of refraction for the longest wavelength radiation encountered must be attained. The range of wavelengths available becomes broader as the index exceeds this minimum. The patent describes graphically the choice of the various construction parameters. D.E.W.

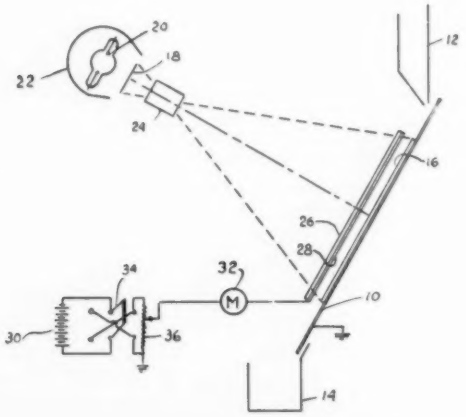


3,057,719 9 Oct. 1962 (Cl. 96-1)
Process for forming electrostatic images.
J. F. BYRNE AND L. E. WALKUP. Assigned to Xerox Corporation. Filed 9 July 1958.

In the basic xerographic process, the powdered particles adhere to the charged portions of the surface, which represent those areas not exposed to light. It is, therefore, a positive process. This invention describes an electrostatic method of reversing the image so that the areas formerly struck by light become charged and will therefore attract the electroscopic marking particles. D.E.W.

3,057,997 9 Oct. 1962 (Cl. 250-65)
Exposure-charged electrophotography.
E. K. KAPRELIAN. Filed 21 May 1956.

The process described differs from xerography in that the latter employs a previously charged surface from which the charge is removed by the action of light, whereas this patent is involved with a process for producing a charge by the action of light. The dielectric copy paper (16) is held against a ground plate and spaced a millimeter or so from a transparent conducting plate (28). The image of the transparency (18) is produced by ultraviolet source 20 and lens 24 of adequate ultraviolet transparency. The action of the light ionizes the air between the plate (28) and the copy paper, producing a charge on the surface of the paper, the exposure being complete when the charging current decays. The image is produced by depositing and fixing powdered pigments as in xerography. D.E.W.

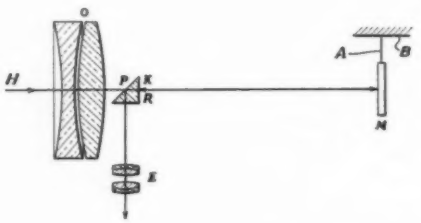


3,058,388 16 Oct. 1962 (Cl. 88-14)
Spectrographic apparatus.
G. W. OGDEN, JR. Assigned to Baird-Atomic, Inc. Filed 1 Mar. 1961.

Two automatic speed-of-scan devices for double-beam infrared spectrophotometers are described. A potentiometer attached to the wavelength drum provides an increasing dc voltage as the spectrum is scanned toward longer wavelengths. This voltage is matched by the output of a tachometer on the wavelength drive motor to provide a slow scan near 3μ and a progressively faster scan toward longer wavelengths. Suppression of the speed when the pen is called upon to move rapidly is provided by adding to the tachometer voltage a voltage obtained by rectifying the unbalanced signal from the pen-servo amplifier. T.K.M.

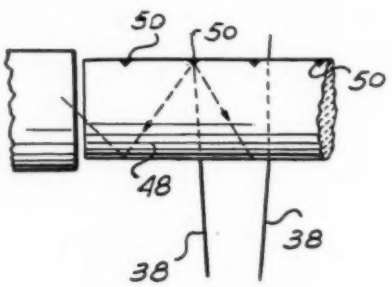
3,059,520 23 Oct. 1962 (Cl. 88-1)
Automatic leveling apparatus.
I. TSUBOKAWA. Filed 26 July 1957 (in Japan 21 Aug. 1956).

A reference crosshair K is placed accurately at the image side nodal point of objective 0. A pendulous mirror M reflects the image to K. The image and crosshair are observed simultaneously on objective E. The crosshair will obstruct that part of the field of view lying on a horizontal line, regardless of slight tilt to the optic axis. When the nodal point is within the objective, the crosshair is placed at the reflected image of the nodal point. Arrangements using both vertical and horizontal pendulous mirrors are shown. D.E.W.



3,060,319 23 Oct. 1962 (Cl. 250-219)
Optical synchronizer.
O. V. GREUNKE. Assigned to United Aircraft Corporation. Filed 8 Dec. 1960.

The purpose of this device is to keep track of the position of a scanning beam such as the one used in the automatic grading of examinations. A transparent rod (48) is scanned by one element of the scanning beam (38). Whenever this beam strikes one of a plurality of grooves (50) cut in the upper side of the rod, light is internally reflected to a photosensitive detector on the left. Suitable counting devices keep track of the location of the scanning beam. Claim 1 reads only upon the elements shown in the figure. D.E.W.



3,060,789 30 Oct. 1962 (Cl. 88-1)
Light-conducting fibers.
J. W. HICKS, JR. Assigned to American Optical Company. Filed 28 Aug. 1958.

The claimant points out that the low index cladding on fibers for fiber optics can profitably have some absorption, particularly in the tube-face configuration where stray light can be a problem. W.L.H.

3,060,792 30 Oct. 1962 (Cl. 88-14)
Optical alignment instrument.
A. N. BRUNSON. Assigned to Brunswick Instrument Company. Filed 16 May 1960.

This instrument constitutes optical tooling for locating points in planes perpendicular to optical lines of sight and points in the lines perpendicular to an optical line of sight. The instrument consists of two accurate orthogonal bearings carrying plane mirrors, so that both perpendiculars to a line of sight can be accurately determined. D.E.W.

continued on page 1180

Measurement of the Infrared Spectral Absorptance of Optical Materials

D. L. Stierwalt, J. B. Bernstein, and D. D. Kirk

The spectral absorptances of some solids have been measured in the 2- to 25-μ region in the temperature range 313 to 473°K by use of a modified Beckman IR-3 spectrophotometer. The emission of each sample is compared directly to a blackbody at the same temperature. Results indicate that this technique offers a most useful tool, particularly for measuring absorption coefficients of low value.

Introduction

Coblentz was a pioneer in the field of infrared emission, absorption, and reflection spectra. Much of his early work, performed in the first two decades of the century, has recently been reprinted.[1] In a series of papers,[2–5] he reported emission spectra of dozens of materials. These spectra were taken at high temperatures (900–1400°C) in the 1- to 8-μ region.

Much information about the optical properties of materials can be derived from emission measurements. It is the purpose of this paper to describe an experimental program (with recent results) for the direct measurement of spectral absorptance of both opaque and transparent materials at moderate temperatures.

Background

In general, when radiation is incident upon an object, part of the radiation is reflected, part is absorbed, and the rest is transmitted. If all of the radiation is absorbed, the object is called a "blackbody". The thermal radiation emitted by such an ideal blackbody is given by the Planck equation

$$W_\lambda(T) = C_1\lambda^{-5}\exp\left(\frac{C_2}{\lambda T}-1\right)^{-1}\ \mathrm{W\ cm^{-2}\ \mu^{-1}}, \qquad (1)$$

where

$C_1 = 2\pi c^2 h$,
$C_2 = hc/k$,
h = Planck constant,
k = Boltzmann constant,
c = velocity of light,
λ = wavelength,
T = absolute temperature.

The authors are with the Infrared Division, Research Department, U.S. Naval Ordnance Laboratory, Corona, California.

Received 31 May 1963.

This is the spectral emissive power of a blackbody. The flux emitted in the spectral band between λ and $\lambda + \Delta\lambda$ is given by $W_\lambda(T)\Delta\lambda$.

For a body that is not a perfect absorber, the spectral absorptance A_λ is defined as the fraction of the incident energy which is absorbed. According to Kirchhoff's law, such a body will emit thermal radiation in the amount

$$W_{0\lambda}(T) = A_\lambda W_\lambda(T). \qquad (2)$$

McMahon[6] has generalized Kirchhoff's law to apply to partially transparent bodies. By considering multiple internal reflections in a plane-parallel sample, he derives expressions for the measurable quantities absorptance, reflectance, and transmittance in terms of the absorption coefficient, reflectivity, and transmissivity. The reflectivity of an object is the fraction of incident radiation that is reflected from a perfect optical surface, while the reflectance includes radiation that has been transmitted by the object and reflected by the back surface. For a transparent material, the reflectivity at normal incidence is given by the Fresnel equation

$$r^2 = \left(\frac{n-1}{n+1}\right)^2, \qquad (3)$$

where r is the Fresnel reflection coefficient and n is the refractive index.

The transmissivity is the fraction of the radiation entering the object that reaches the second surface, while the transmittance is the fraction of incident radiation that emerges from the sample. Since there is reflection loss at both surfaces, the transmittance is always less than the transmissivity. For a plane-parallel sided sample at normal incidence, the following hold when interference effects cannot be resolved[6]:

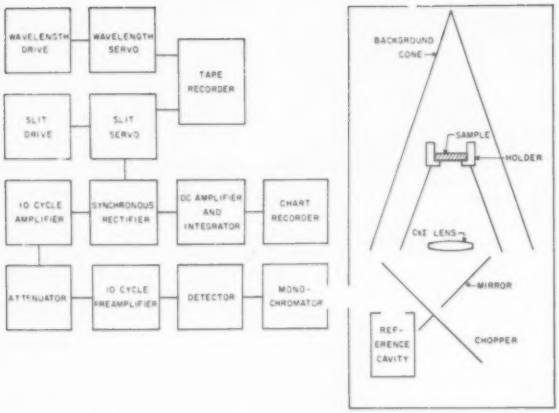


Fig. 1. Block diagram of modified Beckman IR-3 spectro photometer.

$$A = \frac{(1 - r^2)(1 - e^{-\alpha d})}{(1 - r^2 e^{-\alpha d})}, \tag{4}$$

$$T = \frac{(1 - r^2)^2 e^{-\alpha d}}{1 - r^4 e^{-2\alpha d}}, \tag{5}$$

$$R = r^2 \left[\frac{1 + e^{-2\alpha d}(1 - 2r^2)}{1 - r^4 e^{-2\alpha d}} \right], \tag{6}$$

where

A = absorptance,
R = reflectance,
T = transmittance,
α = absorption coefficient,
d = sample thickness.

By adding Eqs. (4), (5), and (6), we obtain

$$A + R + T = 1, \tag{7}$$

which can be verified by thermodynamic considerations.

In the case of transparent materials, the absorption coefficient is a more fundamental property than the absorptance which is a function of the sample thickness. The absorption coefficient can be derived from the absorptance by use of Eq. (4). For small values of αd, Eq. (4) reduces to

$$A = \alpha d. \tag{8}$$

For values of αd of a few percent or less, absorptance measurements can be much more sensitive for determining α than are transmittance measurements.

Apparatus

A Beckman IR-3 spectrophotometer was modified for use in this experiment. The instrument is evacuable, and its temperature is controlled by a water bath system. Figure 1 is a block diagram of the apparatus. The sample is heated by conduction from the polished aluminum holder. Imbedded in the holder are power resistors for heating, a copper vs constantan thermocouple for monitoring the temperature, and a platinum resistance element which is one leg of a bridge regulating the power to the heaters. Radiation from the heated sample is focused on the entrance slit of the monochromator by the cesium iodide lens. The 10-cps chopper has a mirror surface so that radiation from the reference cavity enters the monochromator when the chopper interrupts the sample

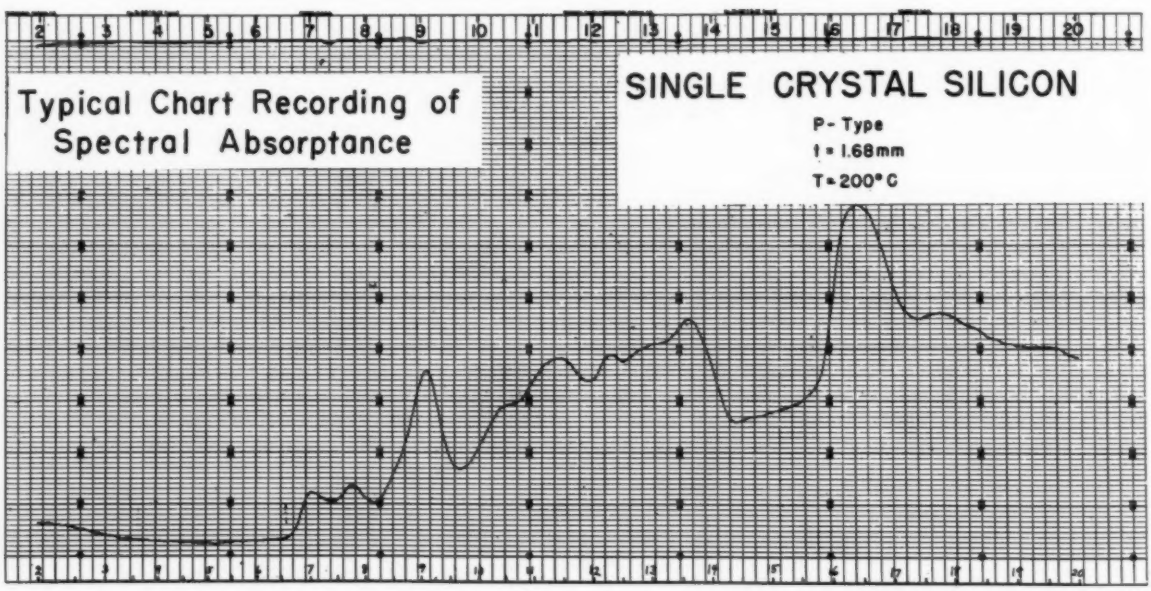


Fig. 2. Typical chart recording of spectral absorptance.

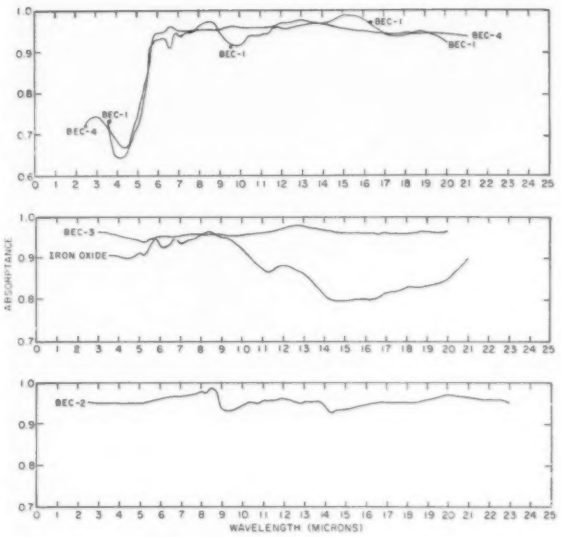


Fig. 3. The spectral absorptance of some blacks.

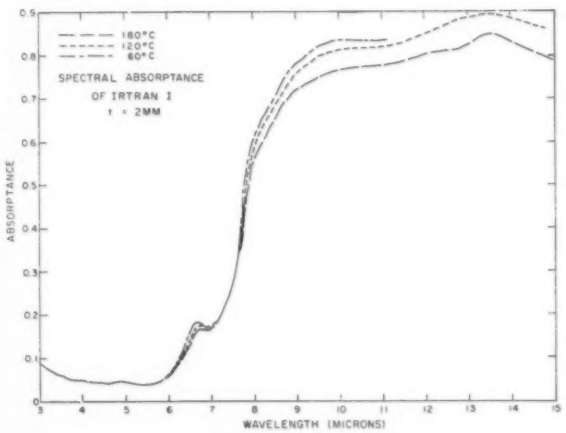


Fig. 4. Spectral absorptance of Irtran 1.

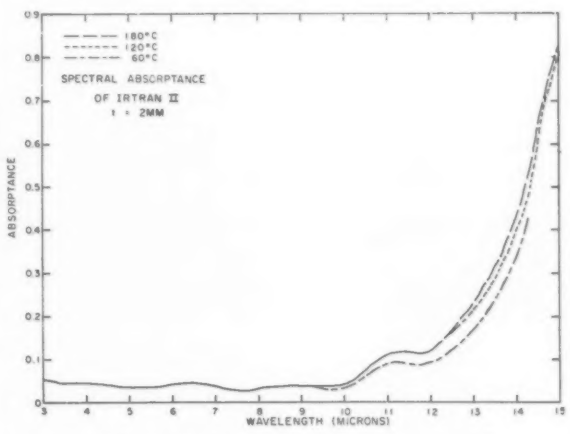


Fig. 5. Spectral absorptance of Irtran 2.

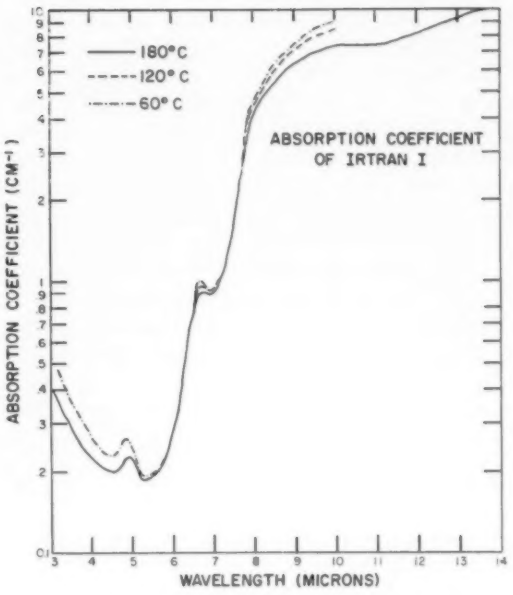


Fig. 6. Absorption coefficient of Irtran 1.

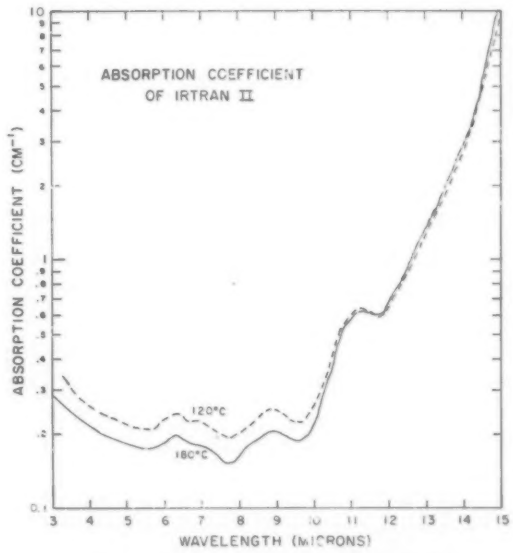


Fig. 7. Absorption coefficient of Irtran 2.

beam. If the reference cavity, background cone, and sample chamber are kept at the same temperature as the monochromator, only radiation emitted by the sample contributes to the ac signal from the detector. For calibration, a blackbody at sample temperature replaces the sample. The absorptance of the sample is given by

$$\epsilon_s = S_s/S_{bb}, \tag{9}$$

where S_s is the signal from the sample and S_{bb} is the

signal from the blackbody. A more general expression for the absorptance has been reported previously.[7]

The Beckman IR-3 has a tape-recorder memory system which can be used to program the monochromator slits. A servo system is incorporated which will maintain constant energy on the detector by varying the slit width. By using a blackbody at sample temperature to standardize the slit program, we make $S_{bb} = 1$ in Eq. (9). Thus, the spectral absorptance is recorded directly on the chart recorder. Figure 2 shows a typical chart recording of spectral absorptance.

The monochromator is equipped with two potassium bromide prisms to cover the spectral region from 2 to 25 μ. Since the measurements were to be made at sample temperatures of 50–200°C, the energy available is a limiting factor. Therefore, the slit mechanism was modified to allow a maximum slit-width of 7 mm.

The detector is a radiation thermocouple with a potassium bromide lens. It is matched to the 10-cycle preamplifier by a 1-Ω to 1-MΩ transformer.

Results

Previously published data have been on semiconducting materials.[7,8] For this report, we have chosen data on materials of more general interest in optical equipment design. Figure 3 shows the spectral absorptance of several blackening materials submitted for evaluation by the Barnes Engineering Company. BEC-1 is a standard black paint. BEC-2 is Sicon black paint. BEC-3 is Krylon flat black paint. BEC-4 is a rather heavy layer of magnesium oxide powder frequently used as a standard white in the visible region. Note that the absorptance scale has been expanded in this figure and does not go to zero. These samples were tested at several temperatures from 50 to 200°C, but since no temperature dependence was noted, only one curve is given for each.

Figures 4–9 present data on a series of hot-pressed materials produced by Eastman Kodak Company: Irtran 1 (magnesium fluoride), Irtran 2 (zinc sulfide), Irtran 3 (calcium fluoride), and Irtran 4 (zinc selenide). In Figs. 4 and 5, the spectral absorptance of Irtran 1 and 2 is given to only 15 μ, the absorptance having been measured with rock salt prisms. Figures 6 and 7 are curves of the absorption coefficients of these materials derived from the absorptance values.

Figures 8 and 9 are curves of 1-mm thick samples of Irtran 3 and 4, taken at 100°C. Transmission measurements confirm that the low absorptance of Irtran 3 beyond 20 μ indicates a high reflectivity.

The absorptance curves of Fig. 10 are for a group of specimens submitted by Servo Corporation of America. These measurements were made at 50°C. A second series of spectra was attempted at 100°C, but two of the samples softened and flowed. These samples were about 1.9 mm thick.

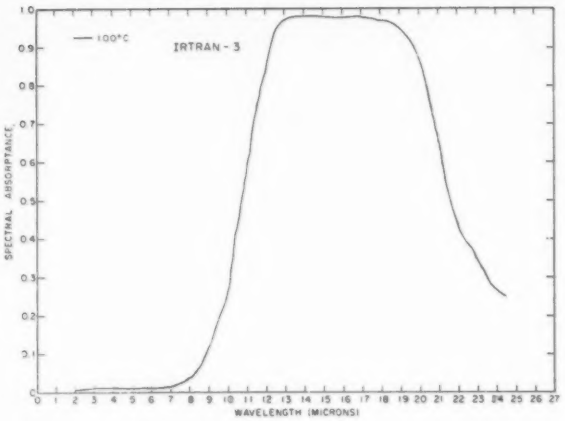


Fig. 8. Spectral absorptance of Irtran 3.

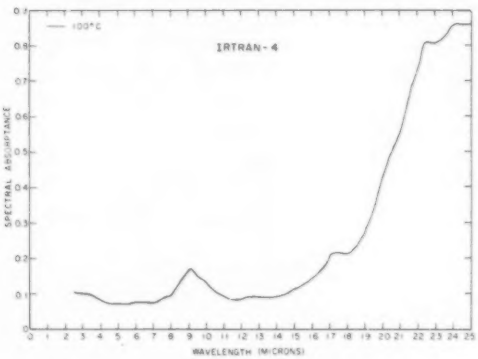


Fig. 9. Spectral absorptance of Irtran 4.

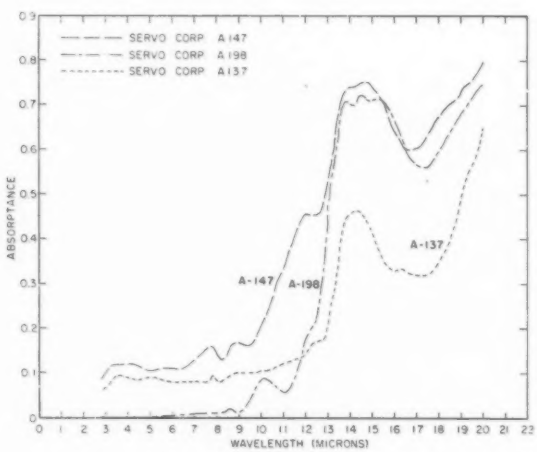


Fig. 10. Spectral absorptance of some glasses.

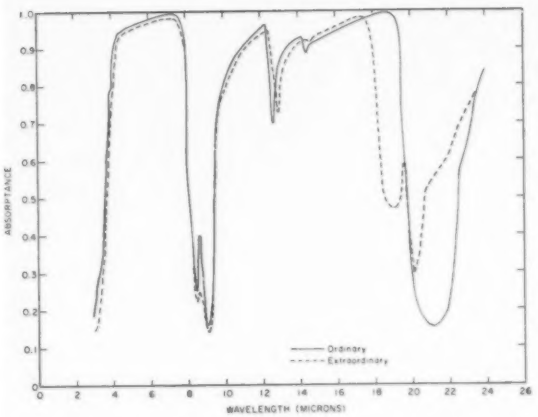


Fig. 11. Spectral absorptance of crystalline quartz at 100°C.

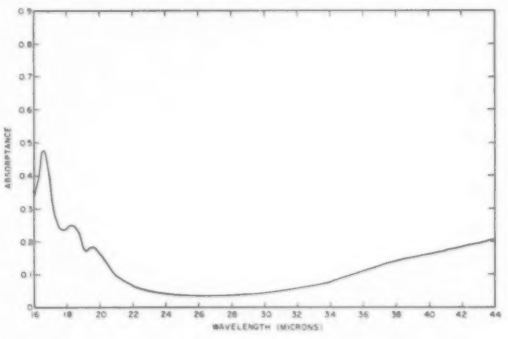


Fig. 12. Spectral absorptance of n-type silicon at 77°K.

A comparison of the absorptance data of crystalline quartz from two orientations, shown in Fig. 11, to reflectance measurements obtained by Spitzer and Kleinman[9] shows good agreement between the two methods of measurement. Spitzer and Kleinman have discarded the small dip at 8.6 μ in the extraordinary ray of their data as spurious. The comparable rise at 8.6 μ in the absorptance data has not been deleted but probably is the result of a slight misalignment relative to the C axis when cutting the crystal.

Future Work

Recently, a second instrument has been fitted with a grating and filters to cover the region from 16 to 45 μ. It has also been provided with a low temperature sample holder. Some preliminary measurements have been made. Figure 12 shows the absorptance of a sample of n-type silicon at 77°K. This specimen was 2 mm thick.

Other modifications planned for the near future are the additions of cooled detectors to both instruments for increased sensitivity and resolution, and the fabrication of cooled sample holder for the first instrument to extend low temperature measurements to about 3 μ.

The authors wish to express their appreciation to Barnes Engineering Company, Eastman Kodak Company, and Servo Corporation of America for making these samples available.

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Of Optics and Opticists *continued from page 1132*

Center was designed to unify facilities and study in science, engineering, and research. Construction of the first three units was facilitated by a $1.25 million grant from the Boettcher Foundation.

Company crumbs . . . . **IBM** announces a new type of transistor in which signals are carried by light rather than by electric current. This optical transistor, made of gallium arsenide and devised by **Richard F. Rutz,** operates on a different principle from a transistor. In the optical transistor, some of the energy of the incoming electric current is converted into light and, after passing through the device, the light is absorbed. Electrons are freed on the output side and pass into the external circuit as output current, giving the effect of current passing through the device. The characteristics of these experimental optical transistors are described in the March Proc. IEEE . . . . A high-precision eucentric-goniometer, designed by scientists familiar with x-ray instrumentation and its needs, is now available from **Electronics and Alloys, Inc.** of Ridgefield, N.J. This device has independent X, Y, and Z motions, arcs designed to eliminate backlash and creep, and many other features which, it is claimed, high-precision x-ray crystallography requires. E & A are a relatively new company, whose scientists were born in Europe . . . . **Cooke, Troughton & Simms, Ltd.** of York, England, have been taken over by Vickers Instruments, Ltd. CTS are well-known mathematical and optical instrument makers . . . . **Zoomar International,** Glen Cove, N.Y., has affiliated with **Ets Pierre Angenieux** of Paris and **Evershed Power-Optics, Ltd.** of London, to act as their exclusive representative for the U.S.A., Canada, and South America . . . A company internal report is available describing the effects of the variation of angle of incidence and temperature on infrared filters. A copy can be obtained by application to the **Optical Coating Laboratory,** 2789 Giffen Avenue, Santa

Rosa, Calif. Its purpose is to assist the engineer to make proper allowances for the effects of temperature and angle on an infrared filter and to provide him with design information which will enable him to set specifications . . . . **Kodak** initiated last year a literature service to keep users up to date with the latest information on Kodak products and their application in day-to-day work. A pamphlet we have seen, "Kodak Materials for Emission Spectrography", is the first installment of this service to those who use photographic materials in spectroscopy. Further pamphlets of interest available to spectrographers are: Gaseous Burst Agitation in Processing (E-57), Some Chemical Reactions in Photography (J-15), Modern Processing for Permanence (J-19), High-Speed Infrared Film (M-9), Ultraviolet Sensitizing of Plates (M-13), Cutting Glass Plates (P-13), and Physical Characteristics of Glass Base Plates (Q-35). To receive these, write to W. F. Swann, Manager, Special Sensitized Products Sales, Eastman Kodak Company, 343 State Street, Rochester 4, N.Y.

Recent **AF** contracts and grants include Electro-mechanical Research, Inc. *Design, Development, Build and Calibrate Rocketborne Ultraviolet Radiometers;* Johns Hopkins U., J. Strong *Far Infrared Spectroscopy* $13,571; U. of So. Calif., Z. A. Kaprielian and R. S. Macmillan *Plasmas and Magnetohydrodynamics and Research in Shockwave Ionization Phenomena Optical Coherence and LASER,* $51,869; Johns Hopkins U., G. H. Dieke *Spectra of Doubly and Triply Ionized Rare Earths* $97,248; City Coll. of New York, E. Erlbach *Infrared Absorption in Strained Silicon* $49,963; U. of Mass., E. A. Soltysik *Study of the Polarization of Light Resulting from the Excitation of Atoms by Electrons* $45,100; Warner and Swasey Co., Flushing, N.Y., H. J. Brabov *Infrared Molecular Band Models, Vibration-Rotation Line-Widths and Strengths* $24,709; Essex Coll., U. of Windsor., L. Krause *Optical Pumping in Alkali-Metal Vapors* $57,198; U. of Ill., P. D. Coleman and R. J. Strain *Studies in Quantum and Solid State Electronics* $57,485; Yale U., V. W. Hughes and W. E. Lamb *Studies of the Properties of Atoms, Molecules, and Plasmas by the Methods of Radiofrequency, Microwave and Optical Spectroscopy* $275,000; U. of Rochester, K. J. Teegarden *Basic Research in Optics* $137,608; U. of Rochester, E. Wolf *Theoretical Studies of Effects of Coherence in Electromagnetic Radiation* $77,219; U. of Colorado, M. Hanna *NMR Studies of Intra- and Intermolecular Interactions* $39,700; U. of Wash., S. Fairball *Study of the Chemical Bond through the Mössbauer Effect* $9250; U. of Ill., D. Holshouser *Problems Related to Optical Communications* $83,718; Baird Atomic, Inc., Cambridge, Mass., B. H. Billings *Circularly Polarized Optical Masers* $49,025; Stanford U., A. Siegman and O. Buneman *Optical and Infrared Masers and Coherent Plasma Phenomena* $109,757; Harvard Coll., D. Hubell, *Neurophysiology of Visual Mechanisms* $10,000; U. of Buenos Aires, E. de Robertis *Ultrastructure and Function of the Retina* $10,000; Columbia U. New York, R. Bershon *Application of Optical Masers to Problems in Chemical Physics* $25,766; U. of Rochester, R. E. Hopkins *Research on Fundamentals of Geometric Optics* $73,500; Optics Technology, Inc., Belmont, Calif., N. S. Kapany *Diffraction and Coherence Phenomena in Optical Waveguides* $31,932; and U. of Paris, F. Abeles *Study of the Optical and Transport Properties of Thin Films of Metals and Alloys* $74,000.

Information for Contributors

Scope: Papers are welcomed in the broad areas of applied optics, in disciplines related to optics and employing optical techniques. Papers should be sent to *The Editor, APPLIED OPTICS,* AFCRL, Bedford, Mass. Manuscripts may be submitted in English, French, German, or Russian, and the presentation should be as succinct as comprehension will permit. In general, the metric system of units is preferred. One original and one carbon copy of the manuscript, with two sets of all illustrations, must be sent in. Manuscripts should be typed double or triple spaced on one side of 22 × 28 cm (8½ × 11 in.) paper, leaving a 3.8 cm (1½ in.) margin all around. Equations must be typed not hand written wherever possible. Papers on the more fundamental aspects of experimental and theoretical optics should be sent to *The Editor, JOURNAL OF THE OPTICAL SOCIETY OF AMERICA,* 68 Hammond Street, Rochester, N.Y.

An abstract, adequate as an index and a summary, of not more than 100 words should appear at the beginning of the paper after the *title, author's name, affiliation, and address.* In the case of papers in a non-English language, they must be accompanied by an abstract in English as well as an abstract in the language of the paper. It should be borne in mind that this abstract may be used in toto by the abstracting journals, therefore it should be self-contained.

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References must be typed on a separate sheet, be numbered consecutively in the order of their appearance in the text, and follow this form:

1. F. C. Brown, Phys. Rev. **12,** 345 (1821).
2. J. Culpeper, *Space Optics* (Georgetown Institute of Technology Press, Washington, D.C., 1861), pp. 12, 345.

A list of abbreviations for the names of journals is published in *Chem. Abstr. List of Periodicals 1961.* To make for uniformity of presentation generally, the American Institute of Physics *Style Manual,* second edition, should be used. In general, *APPLIED OPTICS* differs from the *Style Manual* only inasmuch as footnotes appear at the bottom of the page of text, while references are listed numerically at the end of the paper.

There will be no **page charge** for publishing in *APPLIED OPTICS* for the time being.

Letters to the Editor should follow the above suggestions, but no abstract is required.

The Stressed-Plate Shutter, a New Moderate-Speed Electro-Optical Light Modulator

S. M. Hauser, L. S. Smith, D. G. Marlowe, and P. R. Yoder, Jr.

A new electro-optical shutter system is described which functions by virtue of uniform photoelastic birefringence induced mechanically by piezoelectric means into a glass plate supported between suitably oriented linear polarizers. The basic principles of operation of this stressed-plate shutter are explained in terms of its use as a moderate-speed capping shutter. The suitability of various materials for each of the major mechanical and optical components of the shutter is considered. Design parameters and performance characteristics are given for a working model shutter constructed to demonstrate the system concept. It is shown that, in its present state of development, this type of shutter is capable of closing a 5-cm aperture to an optical density of 3 within 250 μsec of receipt of a triggering electronic signal.

Electro-optical shutter systems have long been employed for high- and ultra-high-speed light modulation and photographic purposes. This is primarily because they operate essentially without inertia and so achieve rapid opening or closure with long useful life. The Kerr cell, Faraday cell, and Pockel cell are the classical examples of this type device. These all have been treated extensively in the literature.[1-4,*]

It is convenient in comparing shutter mechanisms to speak of their "activation time". This is the interval between receipt of the triggering impulse and the completion of the resulting change in transmitted light intensity. The classical electro-optical shutters fall into the nanosecond to microsecond actuation time frame. For certain applications, such extremely fast operation is not necessary but the relatively slow operation of mechanical devices is not adequate since they require milliseconds for macroscopic movement of parts. The use of a complex, ultra-high-speed device in such cases is frequently neither economical nor technically convenient. A gap in available instrumentation thus exists in the microsecond to millisecond actuation time range. The stressed-plate shutter operates in this critical intermediate speed range. It was conceived during a recent search for an electrically driven, submillisecond capping shutter which could be used for a particular military application involving optical telescopes.†

The basic element of all electro-optical shutters is a transparent, optically isotropic material in which birefringence can be induced by some externally applied stress. This element is mounted between linear polarizers which may be aligned with their axes crossed or parallel as demanded by the particular shutter application. When the element is suitably stressed, the state of polarization of the light emerging from it is altered so that it is transmitted or absorbed by the analyzer as the case may be.

In the Kerr cell, the shutter element is a glass chamber containing a pair of flat electrodes immersed in a liquid such as nitrobenzene. A certain voltage applied

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Received 17 August 1962.

This paper is based on two papers on this device read at the October 1961 meeting of the Optical Society of America, Los Angeles, California.

* *Note.* The authors also acknowledge the early work of Hans Mueller and his associates of the Massachusetts Institute of Technology who devised a related, but different, scheme of photoelastic modulation during World War II under military sponsorship. This material was unfortunately not published in the technical literature. For those interested in reviewing the techniques, see United States Letters of Patent of Robert A. Rines and Hans Mueller, Nos. 2,622,470; 2,623,165; and 2,707,749. The work described in this present paper was accomplished independently of Mueller's earlier work. However, the authors gratefully acknowledge the earlier material being called to their attention.

† Work sponsored by U.S. Army Ordnance, Frankford Arsenal, Philadelphia, Pennsylvania.

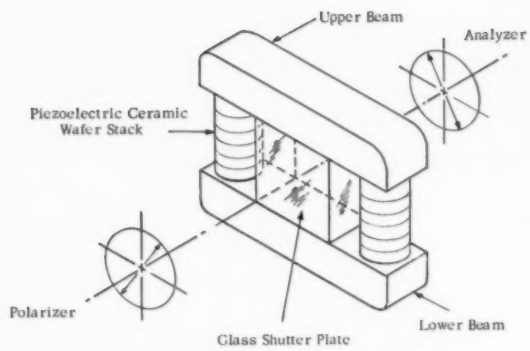

Fig. 1. Major components of the stressed-plate shutter.

between the electrodes produces a half-wave phase retardation of the polarized light which corresponds to a 90° rotation of the plane of polarization. The same effect is produced in the Faraday cell by stressing a cylindrical glass block with a strong, coaxial magnetic field or in the Pockel cell by stressing a crystal wafer with an electrostatic field.

In the stressed-plate shutter, the active element is a glass plate which is made birefringent by an externally applied mechanical stress. The major components of this new shutter are shown schematically in Fig. 1. The plate is cemented between two extremely rigid beams. Mounted between the protruding ends of the beams are stacks of piezoelectric wafers which undergo a microscopic expansion in response to an impressed electrical signal. Mechanical strains produced in the beams by the expanding wafers are transmitted to the plate. The resulting tensional stress in the glass generates the birefringence. This shutter may thus be considered as the mechanical analog to the classical electrostatic and electromagnetic shutters mentioned earlier.

Theoretical Considerations

The relative retardation of polarized light components passing through the plate can be determined from the theory of photoelasticity.[5,6] If the plate material is stiff enough and has a large enough stress-optic constant, the required retardation can be produced by either a compressional or tensional stress applied in one direction only. The tensional mode of operation was found to be best for the particular capping shutter application which is the basis for a large portion of the work reported here.

The magnitude of the retardation in wavelengths may be related to the stress-optic constant, C, of the glass, the plate thickness, t, and the applied stress or force per unit area on the ends of the plate by means of the following equation:

$$n\lambda = Ct\sigma. \tag{1}$$

The load required to produce a half-wave retardation is given by the equation:

$$P = \lambda b/2C. \tag{2}$$

This load is theoretically independent of plate thickness or height but directly proportional to its width b. This has an obvious bearing on shutter design as aperture is of great significance in any practical application. Usually, the tensional load on glass should be limited to about 70 Kg/cm². This then represents a maximum practical limit to P.

The change in length of each of the piezoelectric wafers is, within limits, proportional to the applied voltage and is in the direction of the electric field. In practice, several wafers must be stacked together with electrodes between them so as to produce enough elongation to stress the plate properly. The voltage gradient required across a wafer depends upon its size, its Young's modulus, and its piezoelectric constant

Table I. Pertinent Constants for Several Plate Materials

Glass type	N_D	ν	Young's modulus Y_0(dynes/cm²)	Thermal expansion coefficient α per °C (0° to 300°C)	Stress-optic constant C(cm²/dyne)	Computed load stress at $\lambda/2$ retardation for 1-cm thickness σ(dynes/cm²)	Computed strain at $\lambda/2$ retardation for 1-cm thickness $\epsilon = \Delta l/l$
Borosilicate crown	1.517	64.5	7.96×10^{11}	8.0×10^{-6}	2.81×10^{-13} (2.89×10^{-13})	9.6×10^{7}	1.2×10^{-4}
Light crown	1.523	58.6	7.27×10^{11}	9.4×10^{-6}	(2.76×10^{-13}) (2.82×10^{-13})	9.8×10^{7}	1.3×10^{-4}
Light crown (Hayward C-3)	1.508	61.0	$\sim 7 \times 10^{11}$	5.2×10^{-6}	— (3.63×10^{-13})	— (7.4×10^{7})	$\sim 1 \times 10^{-4}$
Light flint	1.580	41.0	5.54×10^{11}	9.9×10^{-6}	3.18×10^{-13}	8.5×10^{7}	1.5×10^{-4}
Dense flint	1.720	29.3	5.43×10^{11}	7.7×10^{-6}	1.77×10^{-13}	1.52×10^{8}	2.9×10^{-4}
Pyrex	—	—	6.51×10^{11}	3.3×10^{-6}	— (3.88×10^{-13})	— (7.0×10^{7})	1.1×10^{-4}
Fused quartz	1.458	—	7.35×10^{11}	5.6×10^{-7}	3.40×10^{-13}	7.9×10^{7}	1.1×10^{-4}

which is a measure of the strain produced by unit field.

A complication in the design of a shutter of the stressed-plate type is the lack of rigidity of the beams. Two undesirable effects result. First, the wafer stacks have to generate greater strain to bend the beams as well as to stretch the glass plate. Secondly, the curved beams load the plate more strongly at the corners than at the center thereby causing a nonuniform strain pattern across the shutter aperture. Equation (3) gives the deflection, y, in terms of the force, P, exerted upon the plate; the beam Young's modulus, Y_b; and the beam length, z, thickness, T, and height, d. The geometry is symmetrical about the shutter midplane so that each beam undergoes an equal deformation:

$$y = [5P\,(z/d)]^3/[32\,Y_bT]. \tag{3}$$

Selection of Materials

The primary problem in designing a shutter system of this type is that of selecting materials which are compatible with the shutter application and with each other and which have appropriate characteristics so that the required voltage gradient can be as small as possible. Minimizing this gradient facilitates design of the electronic portions of the system and minimizes breakdown or more subtle effects on shutter stability such as saturation or depolarization of the piezoelectric materials. The following equation relates the voltage gradient, E, to the wavelength and the component parameters such as plate width, b; plate stress-optic constant, C; plate and wafer stack cross-sectional areas, A_g and A_c, respectively; plate and wafer material Young's modulus, Y_g and Y_c, respectively; and wafer piezoelectric constant, d.

$$E = \left(\frac{\lambda}{2}\right)\left(\frac{b}{C}\right)\left[\frac{\dfrac{1}{A_gY_g} + \dfrac{1}{2A_cY_c}}{d}\right] \tag{4}$$

The means by which the voltage gradient can be minimized are clear. The shutter plate and wafers should have the largest possible stress-optic and piezoelectric constants, respectively. They should also be as stiff as possible, that is, the product of cross-sectional area and Young's modulus should be as large as possible. Since plate width is determined by the shutter optical aperture required, the base area can be increased only by making plate thickness as large as practical. With a thick plate, the strain required for a given retardation varies inversely with stiffness so that the corresponding strain demanded of the piezoelectric material can, at least in principle, be adjusted to an attainable value. A disadvantage of a thick plate is the increased likelihood of excessive residual strain in the plate which would affect the completeness of shuttering action.

In any practical shutter, careful consideration must be given to stresses introduced into the plate by differential thermal expansion between it, the beams, and the driver stacks. Unless the application allows temperatures to be closely controlled, one must either match the linear expansion coefficients of the different elements in the structure or provide some means of compensating for changes. In all shutters constructed to date, the beams and plate have been rigidly cemented together so the materials used in those components had to be matched thermally. To match three dissimilar materials for plate, beam, and wafers is much more difficult. Hence, compensation appears appropriate. Part of each stack of wafers can be replaced with a spacer or slug of material having such thickness and expansion coefficient as to make the over-all effective expansion of the composite stack match the plate. The defect of this method is that it removes active material from the stacks. Consequently, if a large degree of compensation is required, the remaining active material must be driven at an appreciably higher gradient. To minimize difficulties, it is, of course, advisable to choose all materials with thermal expansion properties as nearly matched as possible.

In order to obtain good optical performance from the shutter plate, it is necessary to use glass for that component. Table I lists various pertinent physical constants for several optical glasses, pyrex, and fused quartz. Most of the data shown were derived from NBS measurements.[7,8] The values shown in parentheses in the C and σ columns are based on measurements made at Electro-Optical Systems on commercially available glass samples similar to the NBS types.

The strain produced in the glass plate as listed in the right-hand column of the table is approximately equal to the change in length per unit length induced electrically into the wafer stack. One can, therefore, estimate the voltage gradient required to produce a given retardation with any wafer material.

The pertinent properties of various wafer materials are listed in Table II. The voltage gradients shown in the right-hand column correspond approximately to a strain of 10^{-4} which was indicated in Table I as a typical value for half-wave retardation in a 1-cm thick plate. Since minimum voltage across the shutter stacks is desired, it is obvious that the first two materials, quartz and tourmaline, are not suitable. Rochelle salt is good from a voltage standpoint but has been shown to be unsatisfactory mechanically.[9] The artificial ceramics of the barium titanate and lead-titanate–zirconate (PZT) types have good piezoelectric characteristics for shutter use. The complex properties of the PZT materials have been disclosed very recently by Berlincourt and others.[10,11] Comparison of their thermal expansion coefficients with those of the glasses mentioned earlier indicates that a match within a few parts per million can

Table II. Pertinent Constants for Several Piezoelectric Materials

Material	Young's modulus Y_c(dynes/cm²)	Thermal expansion coefficient α per °C	Piezoelectric constant $d\left(\frac{\text{m/m}}{\text{V/m}}\right)$	Approximate voltage gradient for strain of 10^{-4} (V/cm)
Crystalline quartz	7.8×10^{11}	1.48×10^{-5}	2.0×10^{-12}	500,000
Tourmaline	2.5×10^{10}	—	1.9×10^{-12}	530,000
Rochelle salt (length expander mode)	2.5×10^{10}	2.80×10^{-5}	2.75×10^{-10}	3,600
Barium titanate	1.0×10^{12}	1.90×10^{-6}	1.90×10^{-10}	5,300
Lead-titanate–zirconate (Type 4)	6.7×10^{11}	2.20×10^{-6}	2.55×10^{-10}	3,900
Lead-titanate–zirconate (Type 5)	5.8×10^{11}	2.20×10^{-6}	3.20×10^{-10}	3,100

be obtained with pyrex or Hayward type C-3 glass. A shutter made of these materials and suitable beams would operate from a voltage gradient of a few kilovolts.

Beam materials are specified on the basis of two physical properties: a large Young's modulus to minimize bending and a coefficient of thermal expansion matching that of the shutter plate material. In Table III physical properties of a few materials which appear suitable for use as beams are tabulated. These materials are listed in order of decreasing Young's modulus. Tungsten carbide, although quite heavy, appears best suited for use as beams. A relatively wide variety of steels is available from which one suitable for use as thermal expansion compensating slugs can be found for most practical applications.

We have found that the bonding materials used to assemble the mechanical structure do not significantly enter into the shutter design, as they are thin layers, and changes in their physical dimensions are small compared to those of other components. Thermal and adhesive properties are, of course, very important. Available epoxy-type cements have been used without undue difficulties. The most important factor is the preparation of surfaces for bonding and the techniques used in the cementing operation.

Table III. Pertinent Constants for Beam and Compensating Slug Materials

Material	Young's modulus Y (dynes/cm²)	Thermal expansion coefficient α per °C	Density ρ(g/cm³)
Tungsten carbide (3% cobalt)	6.79×10^{12}	$\sim 4 \times 10^{-6}$	15.3
Tungsten	3.50×10^{12}	4.3×10^{-6}	19.3
Inconel	2.17×10^{12}	1.1×10^{-5}	8.5
Low carbon steels	2.10×10^{12}	9.4 to 12.2×10^{-6}	7.9
Stainless steels	2.03×10^{12}	9.5 to 16.9×10^{-6}	7.9
Fused quartz	7.35×10^{11}	5.6×10^{-7}	2.2
Pyrex	6.51×10^{11}	3.3×10^{-6}	2.2

Experimental Shutter Design and Performance

The particular combination of shutter materials chosen for use in the experimental shutters constructed for the sponsoring government agency was Hayward-type C-3 plates, tungsten carbide-type 2A6 beams, PZT-4 piezoelectric wafers, and steel compensation slugs. The 2.5-cm thick plates were 5.72 by 6.66 cm with the shorter dimension parallel to the beams. The beams were 11.7 cm long, 2.5 cm thick, and 4.1 cm high. The beams had a T-shaped cross-section selected as a compromise between weight and over-all shutter size. The complete shutter less polarizers is shown in Fig. 2. This shutter assembly weighs slightly less than 3.65 kg.

It is of importance to note the order and manner of assembly of certain shutter components. Since the dimension change of individual piezoelectric wafers is polarized with respect to voltage, there are two ways in which the stacks can be assembled. If the wafer polarities are in electrical series, the capacitance of a stack of n wafers will be $1/n$th and the required stack voltage n times that for an individual wafer. By stacking the wafers so that their polarities are alternating (i.e., electrically parallel), the total voltage is the same as for an individual wafer and the capacitance of the stack is n times the individual wafer value. In this application, recycling time was considered less important than voltage, hence the parallel orientation was used. The 2.5-cm square by 6.3-mm thick ceramic wafers were cemented to conducting electrodes and to the compensating steel slug. The shutter plate and stacks were then cemented to one beam and the second beam cemented to the plate only. A very small gap between the stacks and the second beam allows for any residual differential in expansion and assures that the ceramic will not be loaded when not electrically stimulated.

The functional requirements of the control circuitry should be reviewed briefly at this point since the electrical characteristics affect closure characteristics. The electronics provide the high voltage (about 7 kV) for biasing the shutter into the open condition and the

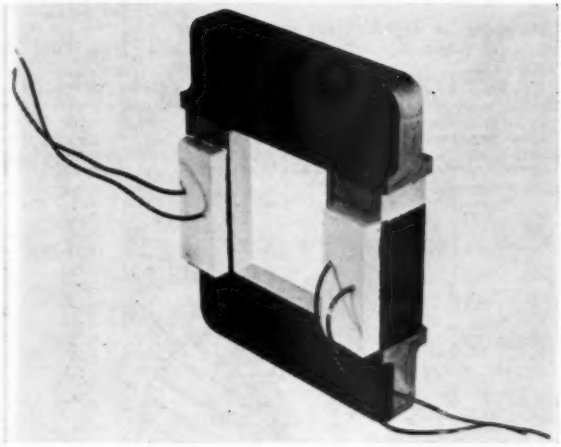

Fig. 2. Photograph of an experimental shutter assembly.

means for shorting out the applied voltage to close the shutter. Since the shutter assembly is rigid, it can be set into resonance by the shock of abruptly removing the bias voltage. For this reason, it is necessary to remove electrical energy at a rate which fails to excite mechanical resonance. This is readily accomplished by discharging the ceramic "capacitors" through a circuit with selected inductance and resistance.

The light-transmission variation during the closure process displays typically a first-order closure within 50–100 μsec followed by a second-order ringing lasting somewhat less than 150 μsec. After this interval, the steady-state light transmission is displayed.

The polarizer types used determine to a large extent the shutter open and closed light transmission, dispersion, and system optical resolution. Sheet linear polarizers, such as polaroid type HN-22, are suitable in the visible spectrum if mounted in glass and supported by a semi-flexible adhesive to prevent the introduction of nonuniform strains in the glass mountings. With HN-22 material mounted in this manner, the open transmission factor is about 10% (density 1), while in the closed state, the transmission is reduced to less than 0.1% (density 3) uniformly over the 5-cm diam optical aperture. Resolution is of the order of 10 sec of arc with available materials.

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Patents *continued from page 1168*

3,060,793 30 Oct. 1962 (Cl. 88-14)
Apparatus for determining ellipticity of surface-reflected plane-polarized light.
A. N. Wells. Filed 22 July 1960.

Describes a simple ellipsometer using two receivers with oppositely oriented polarizers. The ratio of the signals is a measure of the ellipticity induced by reflection at a surface. W.L.H.

3,060,808 30 Oct. 1962 (Cl. 88-65)
Achromatic polarization rotators.
C. J. Koester. Assigned to American Optical Company. Filed 1 Aug. 1958.

Describes achromatic "half-wave plates" made by stacking several half-wave plates at the proper angles. Also describes the way in which such devices can be used with advantage in a variety of optical instruments. *See also* J. Opt. Soc. Am. **49**, 405 (1959). W.L.H.

3,062,086 6 Nov. 1962 (Cl. 88-1)
Block type Albada viewfinder.
F. Papka. Assigned to Voigtlander A.G. Filed 27 Jan. 1958 (in Germany 31 Jan. 1957).

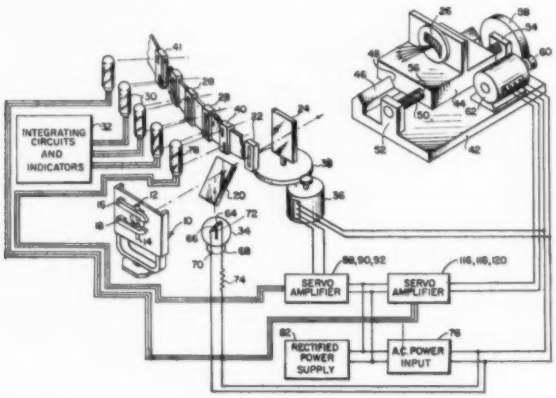
The invention relates to photographic viewfinders of the Albada type in which a frame limiting the image field is reflected into the field of the finder. The patent covers improvements in which the second interface constitutes an eyepiece lens, a reflecting scale is added to the frame-carrying interface, a portion of the system is displaced to compensate for parallax, the viewfinder is combined with a base range finder, and interchangeable frames are arranged to accommodate lenses of different focal length. D.E.W.

3,062,099 6 Nov. 1962 (Cl. 88-40)
Stereoscopic attachment for viewers.
H. W. French, Jr. Assigned to American Optical Co. Filed 12 Feb. 1959.

An attachment is described using plane mirrors which allows a stereo microscope to be used to view stereoscopic picture pairs. W.L.H.

3,064,520 20 Nov. 1962 (Cl. 88-14)
Spectroscopic apparatus.
J. L. Saunderson and E. Dubois. Assigned to Baird-Atomic, Inc. Filed 27 Oct. 1960.

The monitoring light and exit slits of patent 3,056,330 are used in servo systems which simultaneously adjust the dispersion by translating the grating 26 and the grating orientation, by turning a plane parallel plate 24 near the entrance slit 22. Monitoring light from a special mercury tube 34 is introduced at the spectrometer entrance slit. The monitoring exit slit 41, illuminated by a mercury line at the end of the focal range, controls the dispersion. The exit slit 40, next to the entrance slit, controls orientation. (See patent 3,056,330 reviewed in the May 1963 issue, p. 549.) T.K.M.

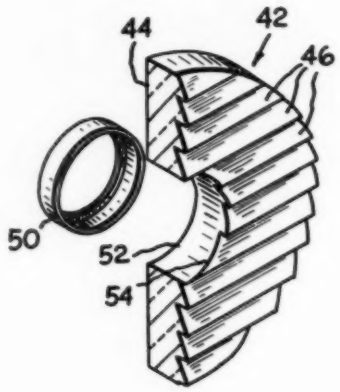


3,065,089 20 Nov. 1962 (Cl. 106-52)
Manufacture of glass.
E. Hustinx. Filed 1 Dec. 1958 (in Netherlands 3 Dec. 1957).

A method of manufacturing by using alkali silicates along with bivalent and trivalent silicates is described. Sodium silicate is reacted with some other salt, calcium chloride for example, in aqueous solution. The resulting silicates are then dried, mixed in the proper proportions, and melted in a suitable mold to form a transparent glass. The melting temperature of the reacted silicates is always substantially lower than that required by conventional methods of making glass. In addition, coloring oxides in the starting materials are removed by the method. In certain cases, organic materials, i.e., silicones, rubber-like materials, and polyvinylchlorides, are added. If the mixture melts below the decomposition temperature, a resilient mass having a glassy appearance is obtained. G.W.C.

3,064,523 20 Nov. 1962 (Cl. 88-24)
Illuminating arrangement for optical devices.
R. J. Meltzer. Assigned to Bausch & Lomb, Inc. Filed 24 Feb. 1960.

The prismatic element shown is located midway between the objective lenses in a telecentric afocal relay system. The prism elements bend the light from an illuminator disposed at an angle to the main optical system. The illumination passes through one objective and thence to the work piece. It is claimed that this element is much easier to adjust than a plane diagonal mirror. The light source should be adequately large so that color effects will be averaged out. D.E.W.



3,065,090 20 Nov. 1962 (Cl. 106-52)
Method of preparing glass.
R. W. Hopkins. Assigned to Pittsburgh Plate Glass Co. Filed 11 May 1959.

This invention describes a method of preparing batches for glassmaking by mixing the sand with an aqueous solution of alkali metal salts, often a solution of sodium carbonate, then adding and mixing the remainder of the batch ingredients and melting the batch to form a glass. It is said that this procedure produces an alkali coating on the sand particles, providing more intimate contact and greater heat efficiency in the melting operation. Among the advantages claimed for this procedure are: dusting in the mixing and conveying operations is reduced; the quality of the glass is improved and rejections due to blisters, seeds, and stones are reduced; melting time is decreased providing increased furnace capacity; life of the refractories in the melting furnace is increased; and the uniformity of the batch is improved. G.W.C.

3,066,575 4 Dec. 1962 (Cl. 88-57)
High-aperture photographic objectives with a small field angle.
J. Mukai. Assigned to Canon Camera Co., Japan. Filed 21 Sept. 1960.

An *f*/1.8 double-Gauss objective is described which covers ±15°. The front component comprises three single elements, the second and third being in edge contact. The rear component contains a thick negative meniscus element followed by a thin biconvex positive element. One example is given, which is limited by eight inequalities. R.K.

3,069,972 25 Dec. 1962 (Cl. 88-57)
Optical system for zoom binoculars.
R. E. Tibbetts and D. C. Gilkeson. Assigned to Revere Camera Co. Filed 25 Jan. 1961.

An optically compensated zoom system is used as the objective of a prism binocular, the range of focal lengths being 143 to 214 mm (1.5 to 1). Focusing is accomplished by the addition of an adjustable focusing collimator in front of the zoom objective. To secure the necessary high correction for spherical and chromatic aberration, the front moving zoom component is a simple convex element, but the rear moving component is a single lens followed by a cemented doublet. The stop position is not specified; it is probably at the fixed intermediate negative element. R.K.

3,074,316 22 Jan. 1963 (Cl. 88-57)
Highly-corrected optical objective.
A. Cox and I. C. Sandback. Assigned to Bell and Howell Co. Filed 20 Mar. 1959.

A 4-element *f*/2.5 objective is described comprising in order: A front positive element, a stop, a biconcave element, a positive meniscus element concave to the front, and a biconvex rear element. Two numerical examples are given, which are controlled by 8 inequalities. R.K.

Study on the Fabrication of Aspherical Surfaces

Takemaro Sakurai and Kōrō Shishido

Various methods of fabricating aspherical surfaces are described in detail. In the method of successive approaches by tools, the figuring procedures and the measuring apparatus were studied. In order to get higher figuring efficiency, a grinding machine consisting of a turntable and a profile tracer with a tool was developed. For the fabrication of conic sections, the tracing arm was operated with a linkage. A tracing system by means of a cam, however, was found to be most satisfactory for general aspherical surfaces. The grinding of a deformed thin plate was also found to be an effective technique when the desired surface was nearly in plane.

Most of the optical surfaces hitherto constructed are those spherical ones that include a plane surface as a limiting case. It is known that the characteristics of a system may be much improved by replacing the spherical surface in the system with an aspherical one. As the spherical surfaces have already formed the systems in fairly good quality, the aspherical surface introduced may be considered to have an axial symmetry and a profile very near to that of a spherical or a plane surface. When the surface required deviates but a little from the spherical one, the deviation may be corrected by a controlled deposition in vacuum. On the other hand, when the deviation becomes rather large, and a fairly good accuracy is required, the surfaces cannot be generated without grinding and polishing. The replica method, useful for mass production, is accomplished with a well-ground and polished mold. It is very difficult, however, to fabricate aspherical surfaces by methods of grinding and polishing. Literature[1,2] on this problem is quite limited, and few reports have been published during the past several years.

Thirteen years ago, an optical workshop was founded at the Research Institute for Scientific Measurements to make optical parts necessary for research and to embody the results of investigation in the real instrumentation. One of the authors (T. S.) was appointed to direct the optical work in the shop. He soon found that, in order to fulfill the duty of the shop, he must develop methods to make aspherical surfaces. Another (K. S.) is the chief engineer and has also worked mainly in this direction. Up to the present, the shop has fabricated a considerable number of aspherical lenses and mirrors. In summarizing this work, they hope to present in what follows some of the procedures used to grind and polish aspherical surfaces.

The authors are with the Research Institute for Scientific Measurements, Tōhoku University, Sendai, Japan.

Received 15 August 1962.

Successive Approach by Tools

For a long time, spherical surfaces have been ground and polished by an iron tool with sufficient accuracy. Therefore, in the fabrication of aspherical surfaces, figuring by a tool with the surface reverse to the required one may be the means to be considered first, which is what we did in the early stage of our investigation. The two cases might seem to be quite similar, but in reality great difference is found between them. Here, we consider the motion of a tool relative to the blank. In the case of a spherical surface, motion along the surface has two degrees of freedom: translation in two orthogonal directions, and translation and rotation about an axis. By grinding, the elevated portion of the blank will be ground off, but, at the same time, the corresponding portion of a tool is also worn away. However, as two degrees of freedom exist, it is possible to make the elevated portion of the blank cover the whole area of a tool surface. Thus the tool can always maintain a spherical form. In the case of an aspherical surface, on the other hand, the allowed motion of a tool relative to a blank in contact is but a rotation about an axis; hence, in grinding, the elevated portion of the blank gives the tool incurable defacements, the degree of which would differ by their relative hardness. Thus the blank figured will have zonal defects symmetrical to the optical axis.

In order to minimize these difficulties, several remedies can be considered. The first is to mold the blank as accurately as possible in order to make the wear of a tool small and even over the whole surface. When the blank is wide and not very thick, it can be formed by

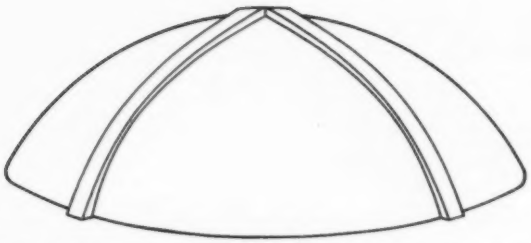


Fig. 1. Tool composed of steel bands fixed on an iron hemisphere.

Fig. 2. Method of fabricating steel bands in Fig. 1.

sagging onto the mold without pressing. For this purpose, diatomaceous earth or graphite is recommended as a mold material. It can easily be figured by a rotating template; it shows little deformation up to the molding temperature. The second remedy to be considered is to make a tool so hard that it does not wear in the grinding. Such a "cure" however, can hardly be realized in practice, and, moreover, the harder the material, the more difficult it is to figure the tool.

The next possibility is to provide many tools and change each one as it is defaced. The difficulty of this method is in the fabrication of many aspherical tools. For this, we tried the following procedure, when we made a paraboloidal mirror, 40 cm in focal length and 70 cm in diameter. To make a tool, steel bands were curved and fixed on a well-ground iron hemisphere in the radial directions, as is shown in Fig. 1. These bands have a thickness which differs in longitudinal direction to have the values equal to the difference between the profile of the paraboloid and that of the hemisphere. Hence, the upper surface of the fixed bands forms the required aspherical surface. As each band is worn out by the grinding, it is replaced by a new one. The steel bands are fabricated by using a mold M, illustrated in Fig. 2. The mold has a stepped upper surface, the envelope of which has a depth equal to the thickness of the required band. The stepped form has been chosen for convenience of construction. A band of steel B is bent and fixed on the mold, and its upper surface is ground in plane, as is shown by the broken line. Thus the required bands are obtained very easily.

By the methods mentioned above, the figuring in the early stage can be done effectively, but the accuracy attained by these is less than the desired value in most cases. Greater accuracy is achieved by repeating successively testing and retouching. Retouching is performed by a small flexible tool, such as a thin glass or steel plate, using emery or carborundum as an abrasive while the work is being rotated. The further the figuring proceeds, the finer the abrasive to be used. A good turntable is necessary to minimize the axial asymmetry of retouching. One of the turntables constructed is illustrated in Fig. 3. Circular iron plates D_1 and D_2, ground nearly optically flat, are separated by steel balls B. D_2 is fixed, while D_1 is rotated on an axis A to make a turntable. The axis A is connected to a driving shaft by a rubber coupling which prevents vibration being transmitted to D_1.

If high optical quality is desired, it is convenient to prepare another aspherical blank of the same material which has a form reversed to the required one. In the retouching, both blanks are corrected and then smoothed together. By this, an axial symmetry is made certain. The same material is desirable because then the wear by smoothing is nearly the same in both blanks.

When the surface is figured sufficiently, it is polished by using rouge or cerium oxide as an abrasive. As a polisher, thin pads of pitch backed by a sponge rubber is available. Soft polisher, such as linen or leather, is to be avoided because it gives rippled defects on the surface. The polishing must be even all over the surface so that defacement will not occur from overpolishing a portion.

When the required surface deviates within several

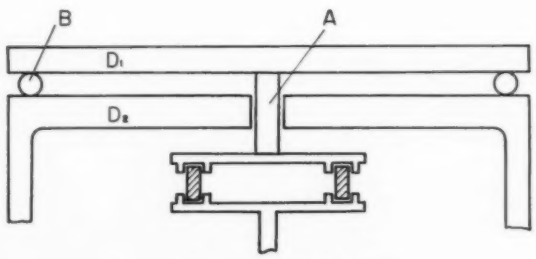


Fig. 3. Turntable.

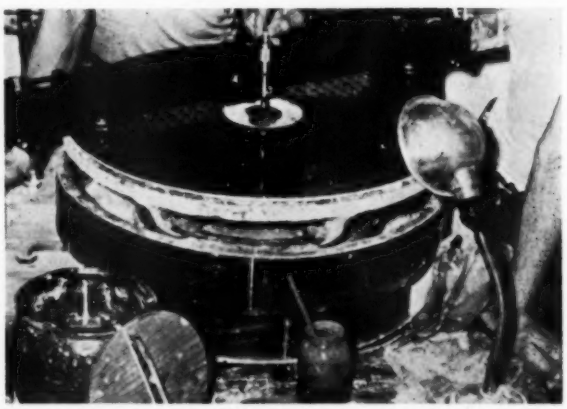


Fig. 4. Measurement of Schmidt lens by means of a micrometer with traveling pods.

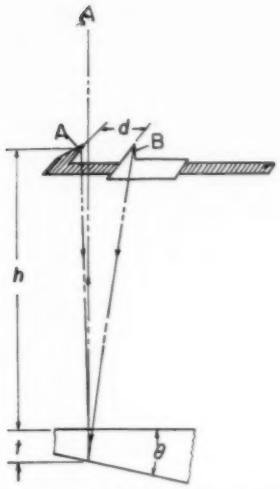


Fig. 5. Method of measuring Schmidt lens by means of a caliper rule.

wavelengths from a spherical one, it can be retouched by polishing only a portion. We applied this method when we fabricated a paraboloidal mirror with a long focal length for a Schlieren optical system. If the retouching is to be effective, it should be ascertained previously by testing how thick a layer of material is worn down in a unit time by polishing under the same conditions.

The most important problem in the successive approach is the measurement of the surface under fabrication. The various methods of measurement should be used in the different stages of the figuring. Here we will describe the means used when we made Schmidt lenses. One of the lenses was for the optical system of a large television projector,* 39 cm in focal length and 0.71 in focal ratio. The working diameter of the lens is 55 cm and the maximum depth of the aspherical surface amounts to about 5 mm. The required resolution of the system is 1/2000 of the focal length on the luminous surface of a kinescope. Taking n as a refractive index of the lens, it gives for the inclination of the aspherical surface a tolerance of $1/2000(n-1)$, which becomes approximately 1/1000 rad. A measuring apparatus used in the early stage of figuring is illustrated in Fig. 4. On a rail of high quality, two traveling pods, placed on a certain zone of the aspherical surface, are mounted. The depth of the zone relative to the center can be measured by a micrometer fixed at the center of the rail. In the last stage of retouching, an optical method was used for the test. For this, the surface was roughly polished and then wiped with an oilcloth to improve visibility. Here one should not polish only portions of the surface, because the effect of abrasive is depressed in the polished portion in the following smoothing. The method of the test is quite simple. As is illustrated in Fig. 5, a caliper rule is held above the aspherical surface at the height h and is adjusted so that the fixed leg A, its image by the reflection of the aspherical surface, and the image of the traveling leg B by the reflection of the back surface will be seen coinciding with each other, and the distance between the legs d is read. Let the inclination and the distance between two surfaces at the reflecting point be θ and t, respectively, and the refractive index of the glass be n. When θ is not large, it can be shown by simple calculation that $\tan\theta$ is given by the following equation:

$$\tan\theta = \frac{1}{2n}\frac{d}{h + t/n}.$$

Taking h as 50 cm, and n as 1.5, 1/1000 of $\tan\theta$ corresponds to 1.5 mm of d. As the value of d is given to a fraction of mm by means of a vernier, sufficient accuracy of measurement can be obtained. The inconvenience of the reflecting method is that not the depth but the inclination is given. It is not difficult, however, to find from the result in what way the subsequent retouching is to be done. Figure 6 is a view of the completed television projector equipped with a kinescope.

Another Schmidt lens was fabricated for a camera, 40 cm in focal length and 2 in focal ratio. In this case, three kinds of measuring apparatus were used in the different stages of figuring. In the apparatus shown in Fig. 7, the depth of the surface is given by a micrometer that travels on a glass rail polished nearly optically flat. Glass rail is convenient because it is free from aging and

Fig. 6. Television projector equipped with a kinescope.

* Constructed at the request of NHK.

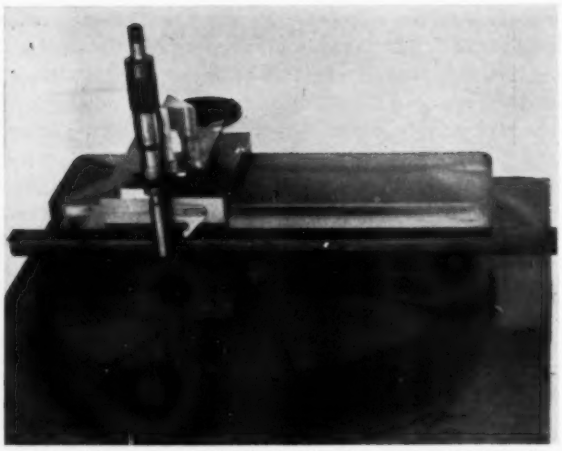


Fig. 7. Measurement of Schmidt lens by means of a traveling micrometer.

its flatness can be examined interferometrically. The surface in the retouching hardly gives a reflecting image at normal incidence, but the visibility of an image is much improved at grazing incidence. Using this feature, a measuring apparatus has been constructed (see Fig. 8). A quartz fiber is stretched tightly to the aspherical surface along its diameter, and the visual distance between the fiber and its image is measured by the microscope provided with a scale in the ocular. Let F and F′ be a point on a fiber and its virtual image, respectively, and let N be the nodal point of the objective lens of the microscope. If the distance between a fiber and an aspherical surface is represented by d, FF′ becomes $2d$. The optical axis of the microscope is assumed to be inclined, with the angle θ to the plane normal to the axis of an aspherical surface. If the line FC is drawn normally to FN to intersect F′N at C, its length s becomes the virtual distance of FF′. Taking t as the distance between F and N and ϕ as the angle between FN and F′N, we obtain the equations as follows:

$$\frac{s}{2d} = \frac{\sin(\pi/2 - \phi - \theta)}{\sin(\pi/2 - \phi)}$$

and

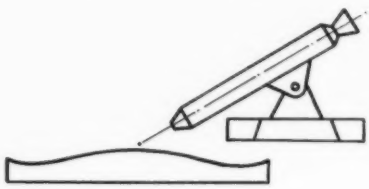
$$\tan\phi = s/t.$$

From these equations,

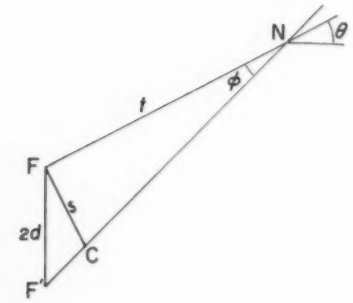
$$\frac{s}{2d} = \cos\theta - \frac{s}{t}\sin\theta,$$

and if θ is chosen to be 30°,

$$d = \frac{st}{\sqrt{3}\,t - s}.$$



(a)



(b)

Fig. 8. Arrangement of measuring Schmidt lens by means of a microscope (a) and its optical diagram (b).

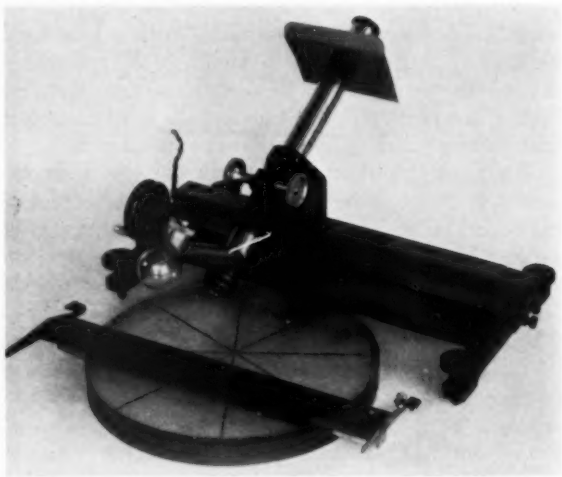


Fig. 9. View of the measuring apparatus given in Fig. 8.

Thus, d is obtained by measuring the value of s. The view of the instrument is reproduced in Fig. 9. For the final measurement of the Schmidt lens, the usual interferometric method shown in Fig. 10 was used.

When the aspherical surface is very near to the spherical one, the best testing method in the retouching stage is to measure the distance between the surface and the center of the sphere. For measuring the polished surfaces, the interferometric method and Foucault test can be used. Since these are well known, no further description will be given here.

Grinding Machine by Means of Linkage

The method of successive approach described in the preceding paragraph gives excellent optical surfaces if

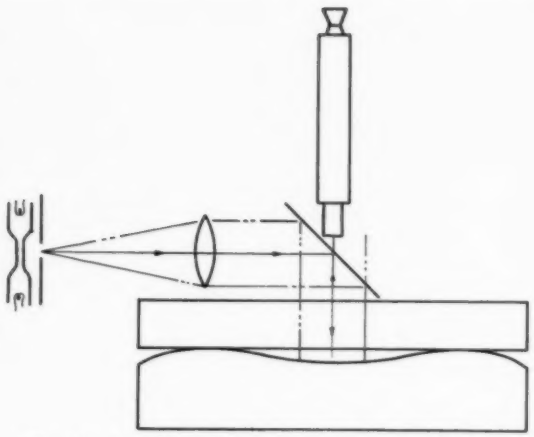


Fig. 10. Interferometric measurement of Schmidt lens.

the time of fabrication is put out of the consideration, but it requires laborious work even if aided by useful measuring apparatus. Therefore, with the lapse of time, our attention has been directed toward finding other more effective and convenient methods. It is an important point that the surface here concerned is symmetrical about an optical axis. It implies that, if any mechanism is found to make a small tool trace the profile of the aspherical surface, the required surface can be generated by rotating the work at the same time. In this case, a very hard tool may be available, and if it were worn out the error introduced could be corrected at any time by adjusting the position of the tool. In such a system, the quality of the ground surface is governed by the function of a turntable and a profile tracer. Such a turntable as is illustrated in Fig. 3 gives sufficient stability in most cases; hence the thing to be done is to determine a system that traces the profile as accurately as possible.

Among various systems, a linkage was first adopted; one used to fabricate a paraboloidal mirror is diagrammatically illustrated in Fig. 11. In this figure, X is the optical axis; p, the parabola that makes the profile of the required surface; F, the focus; and d, the directrix. It is well known that, if a perpendicular to the directrix is drawn from a point on a parabola p, its length PD is equal to the length PF. Here, we consider a link as is shown in the figure, in which F is fixed and D moves along the line d while PD is held always perpendicular to d. A pantograph GHIJ maintains the length PD always equal to PF; thus, the point P, and hence any point in the extension of DP, makes a parabolic track. When a parabola with different focal length is desired, the point F should be displaced along the optical axis. One of the tracers constructed is shown in Fig. 12. Because of the clearance of the couplings, and for other, reasons, the traced track showed a small deviation, but its value was found not to exceed a few microns. Hence the accuracy is tolerable when the mirror to be fabricated is not so high in quality. This system is convenient since it is simple in mechanism and easy to construct; it has a definite defect in that the profile to be traced is limited to only one kind. When the profile is a conic section, a similar link system can be constructed; but when it has a complicated form, hardly any linkage can be applied. Thus, more versatile methods were investigated and resulted in finding the system described in the following paragraph.

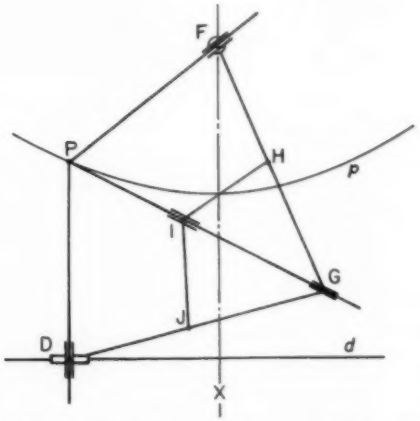


Fig. 11. Profile drafter by means of linkage.

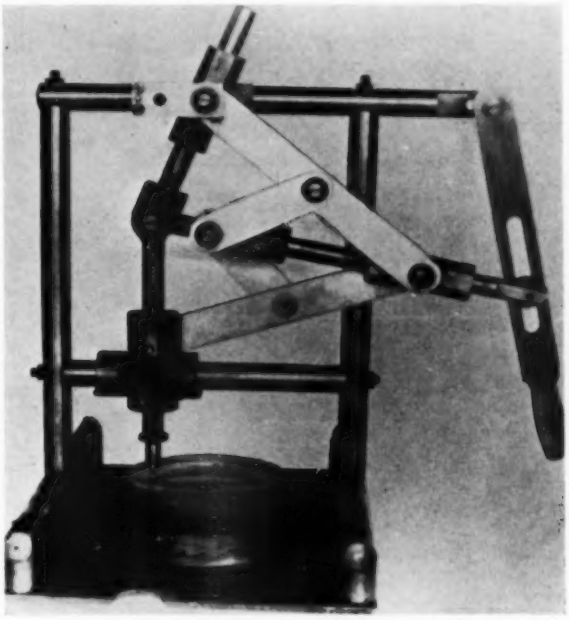


Fig. 12. View of the profile drafter given in Fig. 11.

Grinding Machine by Means of a Cam

The principle of the grinding machine by means of a cam is diagrammatically illustrated in Fig. 13, in the

case where the surface to be fabricated is near to a spherical one. In this figure, X is the optical axis of the desired surface, and B is a pendulous bar which rotates about a horizontal axis A fixed on a point on the optical axis. At the lower end of the pendulous bar, there is a carrier S which can move in radial direction. T is a small tool fixed to the carrier, C is a cam, and R is a small roller which contacts the cam and is connected to the carrier. As the bar inclines from the vertical position, the carrier is displaced by the cam as much as the difference between a spherical and an aspherical surface in this direction. Thus, a tool on the carrier traces the profile of a required surface.

This method was used for the first time when we

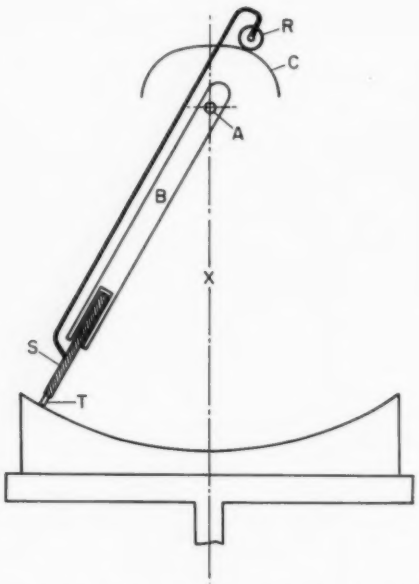


Fig. 13. Principle of the grinding machine by means of a cam.

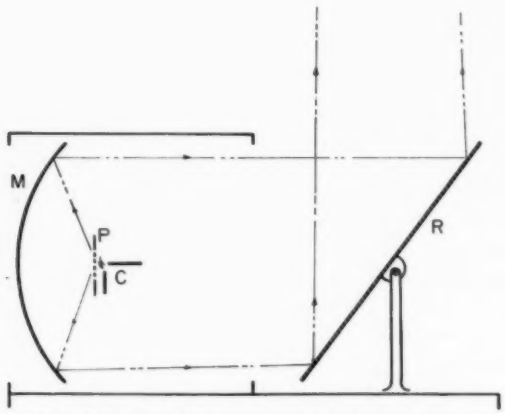


Fig. 14. Optical system of a sky projector. C—carbon arc, P—copper plate in which letters are perforated, M—paraboloidal mirror, R—plane mirror.

Fig. 15. First grinding machine by means of a cam. C—cam, A—arm transmitting the displacement of a roller to a carrier at the lower end.

figured a paraboloidal mirror of a sky projector.* This instrument has an optical system shown in Fig. 14 and makes an image of letters which are perforated in a metal plate mounted in front of a carbon arc on a cloud in the sky for an advertisement as shown in Fig. 15. The paraboloidal mirror is 75 cm in diameter and 36 cm in focal length. To make a mirror, a glass disk, 10 mm thick, has been deformed by heating, and its front surface has been figured by the grinding machine. The tool is an iron rod 1 cm in diameter, and the abrasive is emery. At elevated portions, a roller leaves the cam which prevents the cam from being damaged. The smoothing and polishing used is similar to what we have described in the preceding paragraphs. Little effort has been made for figuring a cam; nevertheless, the mirror fabricated showed an accuracy sufficient for this purpose since the confusion circle at the focal point arising from the imperfection of the surface was about 0.8 mm in diameter. The projecting scene of the apparatus is reproduced in Fig. 16.

The unexpected success in this method has prompted

* Constructed at the request of Morinaga Confectionery Company.

us to construct a second grinding machine to fabricate an ellipsoidal mirror which is used in an infrared spectrophotometer to focus the light from an exit slit onto a detector. The mirror to be made is 12 cm in aperture and has the foci at distances 6 cm and 60 cm, respectively. Figures 17 and 18 represent the construction and the appearance of the grinding machine. In Fig. 17, P is a pendulous bar, C is a cam, and R is a roller which is connected to a carrier S by an arm A. A carrier S is connected to a minimeter G, by which the ground surface can be measured very easily. A turntable T rotates a glass blank M at 50 rpm. In preparation, M is ground in sphere, which contacts the required ellipsoid at the center and intersects it at the circumference. In Fig. 19, the difference between the sphere and the ellipsoid is plotted against the inclination of the pendulous bar θ. As a tool, a small diamond piece, a few millimeters in size, was used. Because of the smallness and the low velocity of the tool, the grinding

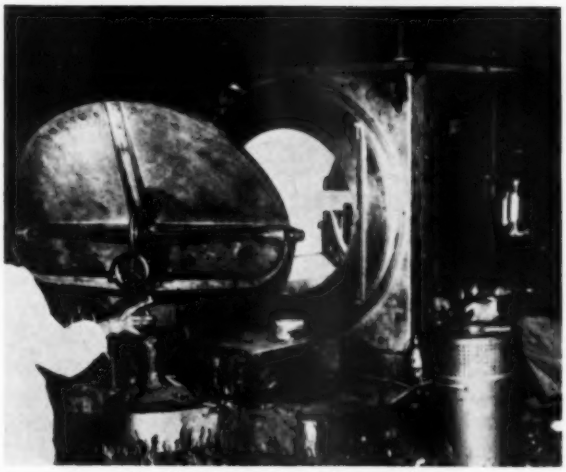


Fig. 16. Sky projector in operation.

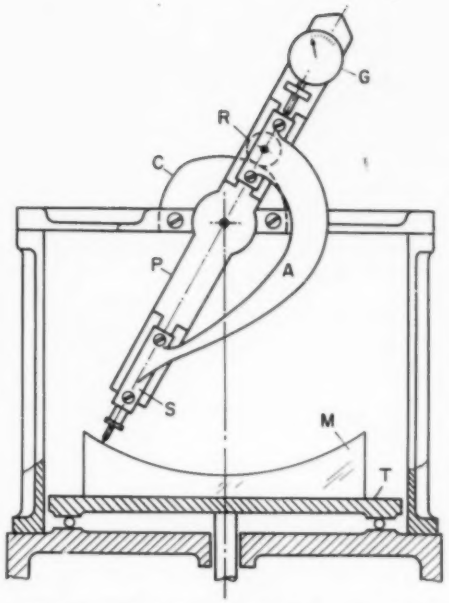


Fig. 17. Second grinding machine by means of a cam.

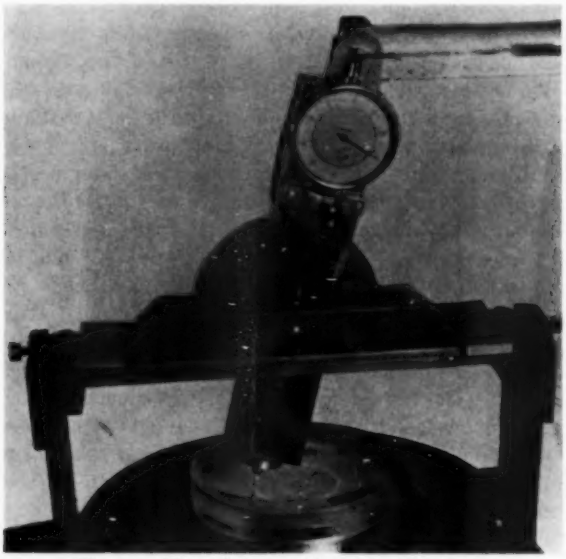


Fig. 18. View of the machine given in Fig. 17.

in a single course was limited to a fraction of $^1/_{10}$ mm; thus several hours were required to finish the whole surface. The mirror fabricated showed a confusion circle of 0.05 mm in diameter at the shorter focus; hence, the accuracy obtained will be satisfactory for this purpose.

In order to develop this method further, we have found some points to be considered. In the machines described above, the accuracy of the ground surface being governed by that of a cam directly, precautions must be taken when a cam is figured. To eliminate this inconvenience, a cam was made in a much exaggerated

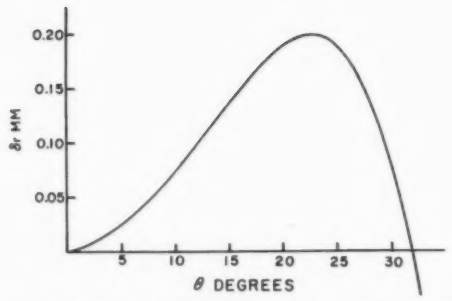


Fig. 19. Difference between the ellipsoid and the sphere, plotted against the inclination of the pendulous bar θ.

form, and then the displacement of a roller was reduced by means of a lever to transmit to the tool. Another consideration is getting the higher grinding efficiency which is necessary not only for saving time but also for eliminating the fault associated with the change of temperature with time. Moreover, the ground surface is desired to be finer in order to minimize the smoothing, which has a risk of defacing the surface. These points have been improved by using a revolving diamond wheel as a tool, mounted in an appropriate manner.

Under these considerations, a new grinding machine has been constructed which is illustrated in Figs. 20 and 21. In this machine, a cam C is composed of a double row of bolts mounted on the circumference of a roughly figured plate. By screwing the bolts, the shape of the cam can be adjusted accurately. The displacement of a roller by the cam is reduced to $^1/_{100}$ by the levers L_1 and L_2 and is transmitted to a carrier S which holds a diamond wheel W. A wheel used is 10 mm and 6 mm in outer and inner diameters, respectively. A motor M drives a diamond wheel at a speed of 6000 rpm. It is mounted not on a carrier but on another arm in order to prevent the vibration from being transmitted to the carrier. The carrier is set slightly declined to the pendulous bar so that the rim of a diamond wheel contacts the blank in the radial direction. The speed of a turntable is about 20 rpm. By this, a smooth surface can be obtained with high grinding efficiency. Using this machine, a paraboloidal mirror 30 cm in aperture and 28 cm in focal length was figured. The mirror is to obtain the collimating mirrors of an infrared spectrophotometer by segmentation. Starting from the nearest spherical surface, the grinding was finished in 20 min. The accuracy of the ground surface was about $\pm 1\ \mu$. The surface obtained was very smooth, and the time required for polishing was about 40 min. All of the three polished mirrors showed a confusion circle less than 0.02 mm in diameter.

Other Fabricating Methods

In this paragraph, other methods of fabricating aspherical surfaces will be described. One of them is that which was used to make a Schmidt camera 40 cm in focal length and 2 in focal ratio. The Schmidt lens is 20 cm in diameter and 52 μ in depth of the neutral zone. Figure 22 shows the procedure how to make the lens. In this figure, M is a mold which has a surface reverse to the desired one. A plane-parallel glass plate P, about 2 mm thick, is bent and cemented to the mold, and its upper surface is ground and polished in plane. By releasing, the lower surface of the plate becomes in plane, and the upper surface makes a desired aspherical form. Thus, if an adequate mold is given, an aspherical surface can be obtained by simple plane grinding. It takes much time and labor to make a mold, but it is not so difficult because the portional overgrinding does not matter in this case if its area is very small. This method is similar to that of Beaven-Wojciechowski, introduced by Brockman,[3] in which a mold is replaced by coaxial rings with different height, fixed on a magnetic chuck, but the result of the test shows that the present one gives more accurate deformation.

In performing this, the surface of the mold and that of the plate were half aluminized to ascertain by interference fringes the degree of contact. Two procedures were used to bend the plate: one was to press the plate with sponge rubber, and the other, to evacuate the air between the plate and the mold. Both were successful. On the mold, grooves were carved to hold the cement. By raising the temperature, the cement spread into the contact surfaces and bound them firmly when the temperature was lowered. The lens fabricated was alumi-

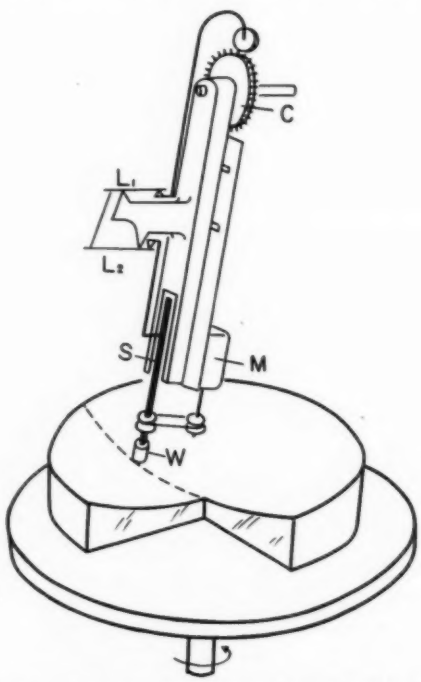


Fig. 20. Third grinding machine by means of a cam.

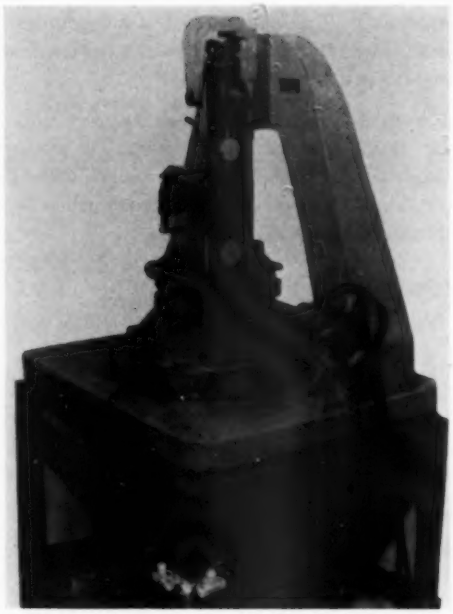


Fig. 21. View of the machine given in Fig. 20.

nized on both surfaces and was examined by the apparatus illustrated in Fig. 23. The number of fringes was counted by the microscope M while the lens was being displaced in lateral direction. The results obtained are given in Fig. 24. The resolution of the completed camera is about 100 lines/mm.

Although this method gives aspherical surfaces very easily, it has a serious defect that the shape of the surface is restricted by the elastic limit of the plate to be deformed. Using a glass plate as thin as 0.6 mm, we could fabricate a lens of a Schmidt camera 18 cm in focal length and 1 in focal ratio, but the work required great care. When plastic materials are available, however, much wider range of the shape can be covered. It must be noted here that the temperature change of the refractive index is not serious because the optical thickness is small and that the shrinkage associated with the molding of monomar does not occur in this case.

Another method of fabricating aspherical surfaces can be added. In the infrared research, it happened that an image of a glober had to be focused on a specimen by a mirror at a large angle of incidence. For this purpose, a spherical mirror with plane back surface was made with plastic blank, and its back surface was bent and cemented to a cylindrical surface of a metal plate. This procedure made a spherical mirror deform into troidal form, and a fairly good image could be obtained.

The aspherization of plane or spherical surfaces by vacuum deposition was also investigated, but it will not be given here because little advance was made from what has been reported by others.

Conclusion

In the preceding paragraphs, various methods of fabricating aspherical surfaces have been presented. What we have intended is to find the procedure suitable for generating the surfaces when a considerable number of of them are required. From this point of view, the method of successive approach is not adequate except when the ultimate accuracy is desired to be extremely high. On the other hand, the grinding of a thin plate in deformed state is effective, as aspherical surfaces can be obtained by simple plane grinding. The lens of this kind is considered to be useful in decreasing the aberrations of various lens systems. For this, a design should be made to improve the system not by aspherizing the surface of a component lens but by inserting a thin aspherical lens nearly in plane.

For figuring general surfaces, the grinding machine composed of a turntable and a profile tracer with a tool is most promising. When the surface required is a conic section, a linkage can be used as a tracer, but it has a definite defect in that the profile to be traced is limited to only one kind. We know that a circle and a linear line are the figures which can be traced with an optical accuracy. Therefore, it is convenient to divide the profile into a circle or a linear line and a deviation which varies along the arc or the line. The most accurate per-

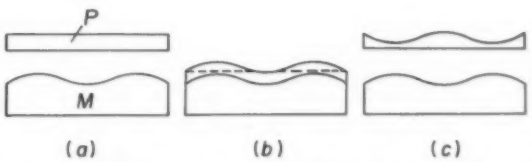


Fig. 22. Fabrication of Schmidt lens by the grinding of a thin plate in deformed state.

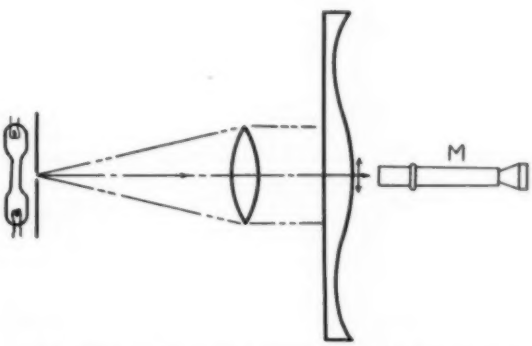


Fig. 23. Interferometric measurement of Schmidt lens.

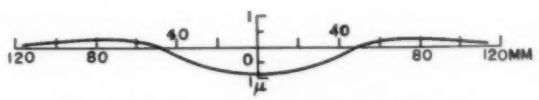


Fig. 24. Accuracy of the fabricated Schmidt lens.

formance of the required deviation would be obtained by the combination of an interferometric and an electronic system which follows a given program. However, our investigation shows that a fairly accurate profile can be obtained by means of a cam. The latter is far more simple and economical than the former. The figured surfaces here presented were restricted to concave surfaces, but convex surfaces may be ground as well. When a surface is nearly a plane, the pendulous bar should be replaced by a carrier which moves on a flat rail in the direction orthogonal to the axis of a turntable. Recently, the component pieces of a paraboloidal mirror 3.2 m in focal length and 10 m in aperture were figured successfully by means of a cam to be used in a large solar furnace. The figuring of a lens which is aspherical and also asymmetrical is being investigated now on the same principle. Their description, however, will be given in a later paper.

The writers express their deep appreciation to H. Tanaka and other members in the optical workshop of the Institute for the continual assistance in this investigation. This work was aided by the Science Research Fund of the Ministry of Education.

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Isosceles Total Internal Reflectors as Optical Elements

Jerome Rothstein

Generalizations are given of the retrodirective "rooftop" and 90° deflecting prisms (called "director" and "deflector," respectively) to angles other than 180° and 90°. The director can be viewed as a combination of two deflectors; a deflector is part of an isosceles triangle prism. In both cases, parallel rays have equal optical paths in the element. There is no change in the direction of the emerging beam when the director rotates about an axis parallel to its ridge. For normally incident rays, achromaticity is achieved in both cases. More than two deflectors can be combined, and deflectors of different angles mixed, to yield totally internally reflecting paths of adjustable direction which are image preserving. Variable path length can also be achieved. For normal incidence, achromaticity is preserved independently of optical path length or direction.

Introduction

The 45°–90° isosceles prism is a well-known element of many optical systems, being commonly used to deflect a light beam through an angle of 90° [Fig. 1(a)] or 180° [Fig. 1(b)]. The latter, sometimes called a retrodirective prism, can be viewed as a double application of the former: the line AA' of Fig. 1(b) divides the prism into halves, each of which functions as in Fig. 1(a). Both kinds of prisms share the property that parallel rays have equal optical paths in the element; the retrodirector has the additional property of directing the incident beam in a path parallel, but in the opposite direction, to that of the incident beam, independent of angle of incidence. As reflections and refractions occur at plane surfaces only, optical images are preserved.

Generalizations of the 90° deflector and 180° director are shown in Fig. 1(c) and 1(d), respectively. In the first the 90° vertex angle is replaced by any angle less than 180°; and in the second, two deflectors, joined along AA', form a generalized director. As in Fig. 1(b), the line AA' can be imaginary, rather than a contact surface. It will be shown that both deflector and director have the property that parallel rays have equal optical paths in the element, and that the director sends the incident beam off in a fixed direction with respect to its initial direction if the director is rotated about an axis perpendicular to the plane of the figure. The limitation on magnitude of angle of rotation is set by the requirement that two internal reflections occur at the surfaces constituting the bases of the two isosceles prisms into which the director is analyzed. The same limitation applies, of course, to the conventional retroreflector of Fig. 1(b).

The present paper has a number of goals. First, we prove the assertions made in the previous paragraph. Second, we show how these and certain additional properties permit the construction of totally internally reflecting optical paths, which are image preserving, of adjustable shape and optical path length, and can also be made achromatic by simple means. Last, some possible applications to optical instrumentation and laser technology are indicated.

Equal Path and Rotational Invariance Properties

Figure 2(a) shows an isosceles triangular prism; DEF is a ray entering at D through a side face, which, after internal reflection by the base face at E, leaves at F through the other side face. It is easy to show that the asserted equality of optical path for a bundle of parallel rays would follow immediately from its validity in the plane case. In Fig. 2(b), where triangle ABC is isosceles with $AB = BC$, E is an arbitrary point of AC. A typical internally reflected ray is DEF. Draw $AG \parallel EF$ and $EH \parallel BC$, intersecting AG in H. The theorem is then proved, if it can be shown that $AH + HG = DE + EF$.

Now $HG = EF$ as the two line segments are opposite sides of a parallelogram by construction. The equality of AH and DE is demonstrated by showing that they are corresponding parts of congruent triangles AHE

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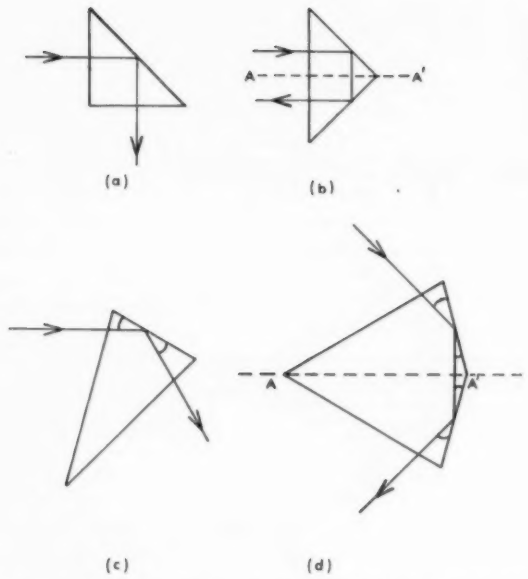

Fig. 1. Deflectors and directors: (a) 90° deflector, (b) 180° retrodirector, (c) generalized deflector, (d) generalized director.

and ADE. The triangles have a common side AE, and $\sphericalangle DAE = \sphericalangle HEA$. These angles are equal because one is the base angle $\sphericalangle BAC$ of triangle ABC, and the other is equal to the other base angle BCA by construction. Lastly, $\sphericalangle DEA = \sphericalangle HAE$, as the former is the complement of the angle of incidence, the latter being equal, by construction, to the complement of the angle of reflection. Congruence thus follows by "angle-side-angle," and the theorem is established.

This equal optical path property is clearly maintained over a chain of deflectors if the intervening media do not destroy it. The condition that this be the case is simply that the exit surface of one deflector and the entrance surface of the succeeding deflector be parallel. It is assumed, of course, that both the intervening media and deflectors consist of optically homogeneous materials. The equal optical path property is maintained for the director of Fig. 1(d), as it can be analyzed into two deflectors with no intervening medium, as discussed earlier.

The image-preserving property is an immediate consequence of the fact that all reflections and refractions occur at plane surfaces. Achromaticity is obtained if the beam enters the first surface normally. A glance at the geometry of Fig. 1(c) shows that the little triangles cut off by the ray are similar. The ray will thus emerge normally if it enters normally, and the condition for equal optical paths ensures that the rays also enter the succeeding deflector normally. An equal path chain is thus achromatic if the beam enters the first surface normally.

It remains to demonstrate the rotational invariance property of the director. It is sufficient, for this purpose, to show, first, that the angle between the portions of the ray within the director before the first internal reflection and after the second one is independent of the rotation angle, and, second, that these portions of the ray make supplementary angles with the director surfaces at the points of entrance and emergence. The second condition implies both that equal angles are made with the normals to the director surfaces (both inside and outside the director) and that changing the angle between entrance surface and ray produces an equal and opposite change in angle between exit surface and ray. Together with the first condition, this would then imply the asserted rotational invariance.

Referring to Fig. 3, let the ray within the director $KHEJ$ be $ABCD$, with internal reflections at B and C, the ray making angles i and j with the base surfaces HE and EJ at B and C, respectively. Produce AB and DC through B and C, respectively, intersecting in G. Denote the base angles of isosceles triangles KHE and KEJ by b, angle HAB by e, and angle JDC by o.

Clearly, triangles AHB and BFE are similar, likewise FEC and CDJ. As BFC is a straight line, e and o are supplementary. Also, from triangle BEC, we have

$$i + j + 2b = \pi \text{ rad.}$$

The angle d between portions AB and CD of the ray is the angle exterior to triangle BCG at G. It is given by

$$\begin{aligned} d &= 2(i + j) \\ &= 2\pi - 4b = HKJ. \end{aligned}$$

This is a constant, equal to twice the vertex angle of the congruent isosceles triangles into which the director is analyzed. The required invariance property is therefore proved.

Applications

There are many obvious applications for directors or deflectors in achieving bent light paths. In general,

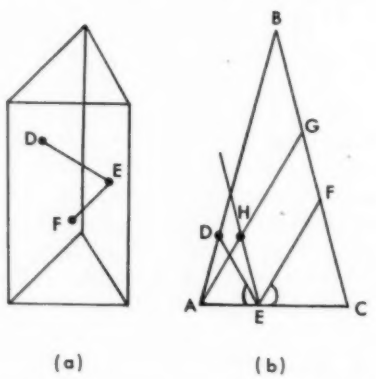

Fig. 2. Equal path property: (a) path of ray in prism, (b) diagram for proof of plane case.

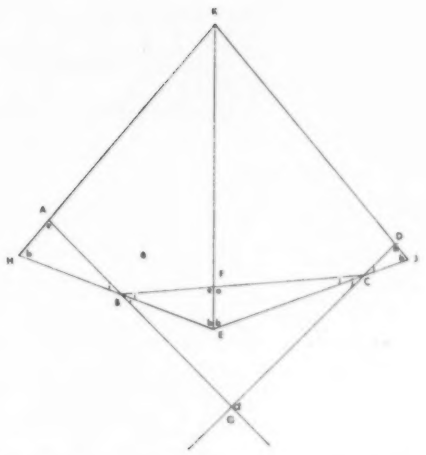

Fig. 3. Diagram for rotational invariance proof.

one might prefer to use them when the combination of antireflection coatings on bounding surfaces and the essentially lossless nature of total internal reflection give an important improvement over lossier metallic reflectors. The angular insensitivity and permanent adjustment of the director angle under unfavorable field conditions may often be attractive. The wide use of 90° prisms also suggests the existence of many applications where other angles might be more convenient.

Of greater interest from the point of view of novelty is the possibility of constructing totally internally reflecting optical paths which are image preserving, free of geometrical aberrations, of shape so easily adjustable as to be almost flexible, of easily varied optical path length, and which can also be made achromatic by simple means. Among the applications which suggest themselves are medical instruments like gastroscopes.

The means of achieving complicated tortuous paths can consist of combined and repeated applications of a few basic optical and mechanical arrangements. While many ingenious arrangements can doubtless be generated for special purposes, we indicate only two simple ones. They have the advantage of yielding the properties enumerated in a simple manner. Figure 4(a) shows how two elements can be connected by a parallelogram linkage. If $AB = CD$ and $AD = BC$, with AD parallel to the indicated exit face of director 1 and BC parallel to the indicated entrance face of prism 2, and pivoting is permitted about axes through A, B, C, and D perpendicular to the plane of the paper, then the equal path property is maintained in spite of the change in path shape consequent to pivoting. In Fig. 4(b) a prism is shown mounted on a bearing; rotary motion about an axis in the plane of the figure and perpendicular to the entrance face is indicated. Motion about pivots or axes of rotation can be controlled by suitable cables from one end of the optical path.

In some cases one might wish to vary the optical path length. This can be done with a suitable telescoping arrangement, e.g., on parallelogram legs AB and CD of Fig. 4(a).

In long systems with many elements, one would want to cut down on losses by using antireflection coatings on entrance and exit surfaces. Alternatively, one could use a fluid of matching refractive index between elements to reduce reflection losses. Refractive deviation of rays is also minimized in this case.

There is no reason why the deflectors or directors in a chain must have the same angles. One can combine elements of different angles into mixed chains or build up elements more complex than directors, which can be analyzed into more than two deflectors. It is possible to design complex elements or chains so that the interesting special properties of the director are preserved (rotational invariance as well as equal path property). The main precaution is to make any given vertex angle appear an even number of times (the vertex angle may exist only on paper, being part of an imaginary dissection of a nontriangular shape).

While all figures until now have indicated the use of full isosceles triangles in the interest of clarity for the geometrical demonstrations, one would not need more than a portion. Referring to Fig. 5(a), if ABC is an isosceles prism and one is interested in the case of normal incidence, then only the portion $DBCEF$ of the prism is actually useful. Similarly, in the director $ABCD$ of Fig. 5(b), the only useful portion for normal incidence is $BCDEFGH$. It is only these portions, or some convenient fraction of the full prisms that includes these portions, which one needs in practice. Only entrance, exit, and internally reflecting faces need be

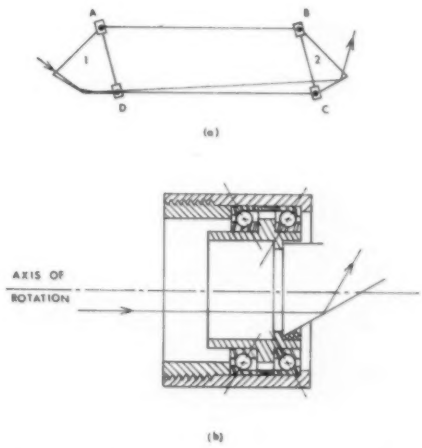

Fig. 4. Simple path change means: (a) parallelogram, (b) bearing.

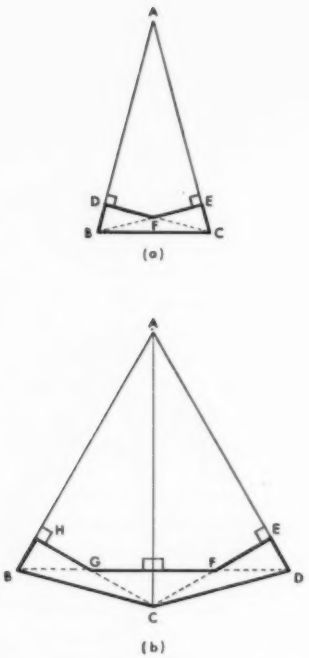

Fig. 5. Useful portions of isosceles optical elements: (a) deflector, (b) director.

fabricated with care; *DFE* of Fig. 5(a) could be replaced by a rough-ground flat surface *DE* approximately parallel to *BC*, and *EFGH* of 5(b) by a rough flat *EH* approximately perpendicular to *AC*.

If the configurations of Fig. 5 are accurately figured, then entrance and exit surfaces are effectively optically parallel. As is well known, optical masers (or lasers) are conventionally constructed from suitable optical materials, e.g., ruby, by making two bounding surfaces suitably highly reflecting and optically parallel. A common geometry is a cylinder whose parallel reflecting ends constitute the two plates of a Fabry-Perot resonator. Faces *DB* and *CE* of 5(a) or faces *BH* and *DE* of 5(b), made suitably reflecting, could function the same way if the elements are fabricated from ruby or other laser material. Fabrication difficulties would, of course, be greater than those of the conventional case because of the greater number of accurately figured surfaces. However, the wide variety of possible shapes for these geometries may permit the use of specimens too small in any one dimension to give satisfactory laser action with conventional geometry. There is also a volume economy for given reflector separation. In Fig. 5(a), for example, the volume *BFC* is traversed both by incident and reflected beams; conventional geometry for the same effective plate separation uses an additional volume of this amount. For scarce experimental materials, which may also contain optical imperfections, the advantages enumerated may, on occasion, more than outweigh the expense and inconvenience of the additional optical work required.

Conclusion

It has been shown that virtually all of the useful properties of the 90° internally reflecting prism can be generalized to other angles. The resulting optical elements should be useful in a variety of optical systems and, possibly, in laser technology.

REFEREES

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Slit-Introduced Errors in Pressure-Broadened Line Measurements

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Electro-Optical Systems, Inc., Pasadena, California.
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There is a tendency for short-arc lamp manufacturers to use prism instruments when obtaining the spectral energy distribution of their lamps. The incentive for using a prism is probably the wide spectral ranges attainable. In using a prism instrument with its widely varying angular dispersion it is easy to fall into error when examining a spectrum characterized by lines and a continuum. A surprisingly large number of investigators are careless in maintaining small spectral slit-widths in order to avoid a serious exaggeration of energy in the neighborhood of lines. These considerations become important in space radiation simulation where the area under a spectrum may represent millions of watts or may represent a heavily filtered source spectrum produced by an expensive instrument.

Noninfinitesimal entrance and exit slits cause a disproportionate increase in the areas under lines compared to areas under the continuum when the spectral slit-widths are of the same order of magnitude as the width of the lines.[1-3] In a two-slit system there are two causes for this misrepresentation. First, the entrance slit produces an impure spectrum, and second, the exit slit intercepts this impure spectrum and integrates a certain spectral band producing further misrepresentation in the sensor signal.

In visualizing spectral impurity it is helpful to consider the entrance slit as being composed of a large number of very narrow, parallel, imaginary slits, each of which produces its own highly pure spectrum in the focal plane of the focusing element. The resulting spectrum can therefore be considered as an aggregate of the overlapping spectra. With one-to-one magnification by the collimating and focusing elements, the spectra produced by the imaginary slits are displaced with respect to one another by the same distances as the relative displacements of the slits producing the spectra. Figure 1 indicates the completely resolved spectral energy curves produced by two infinitesimally narrow slits lying at the edges of both jaws of the entrance slit. If the mechanical slit-width is S and if the plate factor ϕ of the instrument is believed constant over the spectral region being considered, then the two curves represented in Fig. 2 are displaced with respect to one another by a wavelength interval ϕS. Between these two points there is a continuous distribution of identical spectra produced by the other imaginary slits comprising the total mechanical slit width. The spectral energy distribution function occurring at the focal plane of the focusing element is the sum of this inffnite number of completely resolved curves. The spectral irradiance $H_{2\lambda}$ of this sum at a wavelength λ would be the sum of an infinite number of vertically overlapping, infinitesimal elements of area. If these elements to be summed are placed side by side rather than vertically for the summing process, it becomes apparent that the sum can be represented by an integral of the true spectral irradiance curve $H_{1\lambda}$, of the source between the limits of $\lambda + (\phi S/2)$ and $\lambda - (\phi S/2)$:

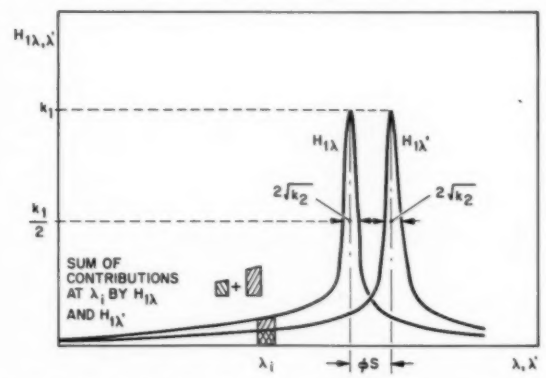

Fig. 1. Focal plane irradiance produced by two imaginary infinitesimally wide slits at either jaw of entrance slit.

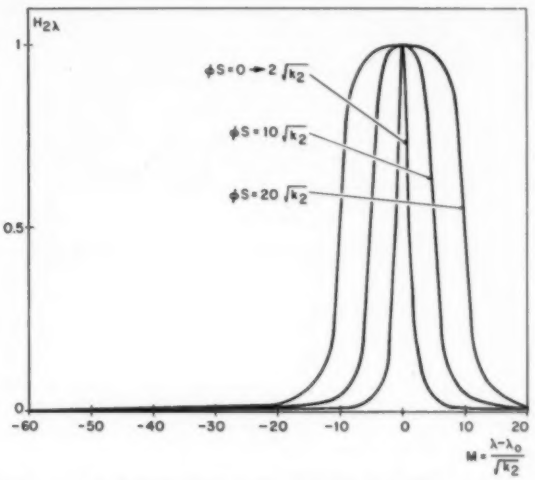

Fig. 2. Focal plane irradiance vs wavelength for various spectral slit-widths.

$$H_{2\lambda} = \int_{\lambda - \frac{\phi S}{2}}^{\lambda + \frac{\phi S}{2}} H_{1\lambda}\, d\lambda. \qquad (1)$$

$H_{2\lambda}$ is the impure spectral energy distribution function which appears in the focal plane and which is intercepted by the exit slit. See Fig. 2.

A convenient mathematical model for a pressure-broadened emission line centered about λ_0, having a half intensity width of $2\sqrt{k_2}$ and a peak of k_1, is

$$H_{1\lambda} = \frac{k_1 k_2}{k_2 + (\lambda - \lambda_0)^2}. \qquad (2)$$

The form of Eq. (2) was chosen because it is integrable in (1); the resulting function $H_{2\lambda}$ is also integrable, and the function $H_{3\lambda}$ which results from integrating $H_{2\lambda}$ is also integrable. Furthermore, it represents the essentials of a pressure-broadened line and its adjacent continuum. The integrations, which can be found in any table of integrals, were done numerically on a computer.

The first integration, Eq. (1), represents the impure spectrum caused by a nonzero entrance slit. This energy distribution would strike a photographic plate if the dispersing instrument were used as a spectrograph rather than as a monochromator. The second integration, Eq. (3),

$$E_{1\lambda} = \int_{\lambda_a}^{\lambda_b} H_{2\lambda} d\lambda \tag{3}$$

is necessary to compare the effect of the entrance slit on rates of growth of areas under lines to areas under adjacent continua for

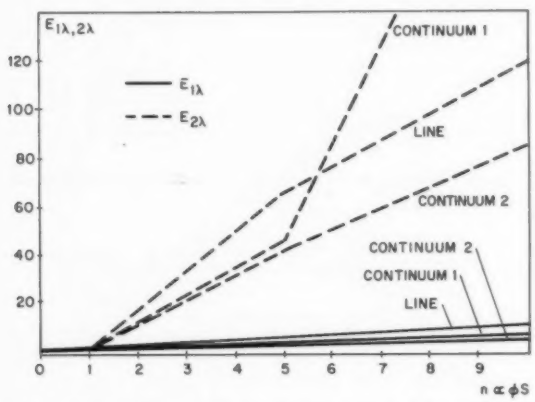

Fig. 3. Rates of change of areas between line limits compared to those areas under two arbitrary sections of the adjacent continuum for various spectral slit-widths.

varying values of ϕS. See Fig. 3. The third integration, Eq. (4),

$$H_{3\lambda} = \int_{\lambda - \frac{\phi S}{2}}^{\lambda + \frac{\phi S}{2}} H_{2\lambda}\, d\lambda \tag{4}$$

represents the integrating effect of a nonzero exit slit-width. See Fig. 4. In this figure, $M = (\lambda_0 - \lambda)/2\sqrt{k_2}$. It is formally the same integration as the Eq. (3) but with different limits. The final integration, Eq. (5),

$$E_{2\lambda} = \int_{\lambda_a}^{\lambda_b} H_{3\lambda} d\lambda \tag{5}$$

is necessary to compare the combined entrance and exit slit effects on rates of growth of areas under lines to areas under adjacent continua for the chosen values of ϕS. The curves were normalized to the same value at $\phi S = 0$ since the ratios of the ordinate values of the three curves are to be interpreted as the proportionate misrepresentation of the areas under the designated portions of the spectral distribution. At $\phi S = 0$ or with infinitesimal slit-widths there would obviously be no misrepresentation in the areas under the spectral distribution. If no exaggeration of the line area existed and therefore if all curves in Fig. 3 were growing at the same rate with respect to ϕS, then all curves would coincide. For zero slit-width the peak normalized function $H_{1\lambda}$ is used. The spectral slit-widths were chosen for convenience so that

$$\phi S = n\, 2\sqrt{k_2},$$

where n is allowed to take on values 10, 5, 1, $^1/_5$, $^1/_{10}$.

Arbitrary line and continuum limits were set up as indicated. Integration of Eqs. (3) and (5) were performed between these limits.

We would like to acknowledge Roger Hughes' assistance in programming and the helpful comments of Don Barry.

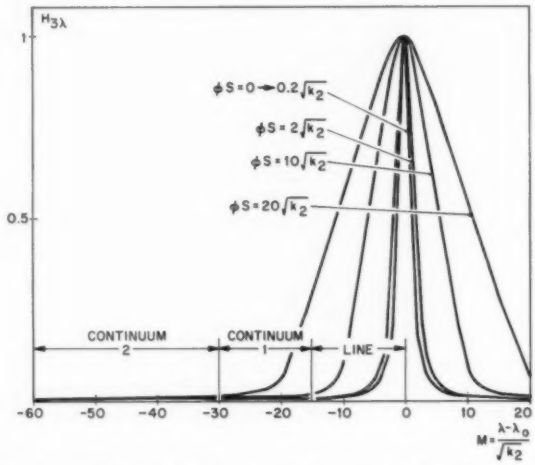

Fig. 4. Irradiance intercepted by exit slit vs wavelength for various spectral slit-widths.

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Errors in Infrared Absorption Measurements Due to Wall Adsorption of Water Vapor

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In a recent article on the total absorptance of water vapor in the near infrared, Burch *et al.*[1] (BFW) touched on one of the most difficult problems of infrared absorption spectroscopy: when a gaseous sample has been put into an absorption cell, how can one determine how much of the sample is actually present in the optical path, and how much of it has been absorbed on the inner

surface of the cell. It is perhaps worth noting that problems of this type were examined at great length by Penner and Weber,[2] albeit not for water vapor. In the case of water vapor it is obviously insufficient to introduce a weighed amount of liquid water into an evacuated cell and then to permit it to vaporize; the BFW study indicated that approximately half of the introduced water was immediately adsorbed on the steel walls of the cell. When water vapor alone is present in the cell it is possible to determine the absorber concentration with some certainty by measuring the pressure of the water vapor, as this is a direct measure of the amount of unadsorbed water vapor in the optical path.

The BFW study discussed this problem in some detail and also discussed the treatment of this problem in an earlier study by Howard *et al.*[3] (HBW), who had endeavored to study water vapor total absorptance in various "synthetic atmospheres", i.e., with nitrogen or oxygen added as a diluent to the sample in order to simulate the earth's atmosphere under various conditions of ground level pressure and reduced pressures corresponding to higher altitudes.

When a diluent such as nitrogen is added to a sample of water vapor in an absorption cell the water vapor pressure can no longer be measured directly. According to the BFW study, "in the HBW work, it was *assumed* that, once an 'equilibrium pressure' had been attained with water vapor alone in the cell, the addition of nitrogen would not disturb the equilibrium between adsorbed water and water vapor; in other words, that the nitrogen even at high pressures would neither displace adsorbed water nor cause additional water to be adsorbed. The validity of this assumption has been questioned, and there has been some speculation regarding the validity of certain of the HBW results for water vapor."

The BFW study introduced the refinement of a dew-point indicator into the absorption cell; in this way it was possible to continue to monitor the amount of water vapor present as various additional pressures of nitrogen were achieved. Dew-point measurements showed no appreciable variations in water vapor partial pressure as long as the cell temperature remained constant. This result indicates that the addition of nitrogen had no significant influence on water vapor adsorption. Thus, according to the BFW study, "the HBW assumption that adsorption is not seriously influenced by the addition of nitrogen would appear to be valid".

We would like to add that in making our previous assumption that the addition of nitrogen would not disturb the equilibrium between adsorbed water and water vapor we had one additional piece of evidence that such an assumption was valid. With pure samples of water vapor alone added to the cell we monitored directly the water vapor pressure and felt reasonably confident that we were thereby free of adsorption effects. When the nitrogen added as a diluent amounted to 1 atm total pressure we were able to compare our absorption spectrum and total absorptance value for the various water vapor bands with the values obtained by other workers,[4,*] who had measured water vapor absorption in long paths in the open air. These values agreed quite well. It seemed to us that with fair confidence in our samples of lowest pressure (the water vapor alone) and at our highest pressure (1 atm pressure), it was not unreasonable to assume that intermediate pressures of nitrogen should not disturb the adsorbed water vapor equilibrium. This was therefore a contained assumption, valid at both extremes, rather than an open-ended one.

The HBW study was made nearly ten years ago, with a much cruder apparatus than that now available for the BFW investigations. We continue to be more surprised by the agreement between the two sets of data than by the differences between them.

* A similar comparison was subsequently made with the data of Taylor and Yates.[5]

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"Push-Pull" Optical Modulators and Demodulators

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In conventional optical amplitude modulators that use crystals exhibiting the linear electro-optic effect, the crystal and a quarter-wave plate are mounted between crossed polarizers.[1,2] The intensity of light I transmitted by such a modulator is given by

$$I = \frac{I_0}{2}\left[1 + \sin\left(\frac{\pi}{V_{\lambda/2}} V \cos\omega t\right)\right], \tag{1}$$

where

I_0 = intensity of light incident on crystal,
V = amplitude of modulating voltage,
ω = angular frequency of modulating voltage,
$V_{\lambda/2}$ = voltage required for full transmission.

Equation (1) shows that the average light intensity transmitted by a conventional modulator is only one-half the intensity of the light incident on the crystal.

Figure 1 shows a schematic diagram of a "push-pull" optical modulator in which the average intensity of the transmitted light *equals* the intensity of the light incident on the crystal. In this modulator, the light transmitted by the crystal and the quarter-wave plate is split into orthogonally polarized components by means of a Foster-Seeley prism. These two components travel along separate paths before they are recombined in a second Foster-Seeley prism. The two cascaded Foster-Seeley prisms can, in principle at least, be replaced by a wave plate with phase delay $(\pi\Omega)/\omega$, where Ω is the optical angular frequency.

The intensities I_h and I_v of the two beams leaving the first Foster-Seeley prism are given by

$$I_h = \frac{I_0}{2}\left[1 + \sin\left(\frac{\pi}{V_{\lambda/2}} V \cos\omega t\right)\right], \tag{2a}$$

$$I_v = \frac{I_0}{2}\left[1 - \sin\left(\frac{\pi}{V_{\lambda/2}} V \cos\omega t\right)\right], \tag{2b}$$

where the subscripts of I refer to the horizontal and vertical direction of polarization of the beams, as shown in Fig. 1. If the path difference of the two beams between the prisms is adjusted to delay the horizontally polarized beam by a time π/ω with respect to the vertically polarized one, the intensities of the two beams leaving the second prism are given by

$$(I_h)_{out} = \frac{I_0}{2}\left\{1 + \sin\left[\frac{\pi}{V_{\lambda/2}} V\cos(\omega t + \pi + \theta)\right]\right\} \quad (3a)$$

$$= \frac{I_0}{2}\left\{1 - \sin\left[\frac{\pi}{V_{\lambda/2}} V\cos(\omega t + \theta)\right]\right\},$$

$$(I_v)_{out} = \frac{I_0}{2}\left\{1 - \sin\left[\frac{\pi}{V_{\lambda/2}} V\cos(\omega t + \theta)\right]\right\}. \quad (3b)$$

The total intensity I_t of the output is, therefore,

$$(I_t)_{out} = I_0\left\{1 - \sin\left[\frac{\pi}{V_{\lambda/2}} V\cos(\omega t + \theta)\right]\right\}. \quad (4)$$

This expression shows that the intensity of the light transmitted by the push-pull modulator is twice that of a conventional modulator.

Similar push-pull schemes can be used to double the output of demodulators for polarization modulated beams. Polarization modulation is produced if the analyzer is omitted from a conventional optical amplitude modulator.[3] Since the intensity of a polarization modulated light beam is constant, such a beam cannot be directly demodulated in conventional optical demodulators like phototubes or photomultipliers. One scheme is simply to put the two Foster-Seeley prisms of Fig. 1 in front of a conventional optical demodulator. A second scheme is illustrated in Fig. 2. In this demodulator, the received beam is split into two orthogonally polarized components, and these two components, which are amplitude-modulated with opposite phase [see Eq. (2)], are fed into separate optical demodulators. The electrical outputs of the demodulators are added in a hybrid ring to produce a power output that is twice that of each individual demodulator signal.

The frequency response of the push-pull demodulator of Fig. 2 is limited only by the response of the optical demodulators and the hybrid ring, and operation with octave bandwidth at modulation frequencies ranging from audio to microwaves is possible with available components. On the other hand, the bandwidth of push-pull modulators using two Foster-Seeley prisms and a single optical demodulator is limited to only a fraction of an octave (since the difference in path length of the two beams between the Foster-Seeley prisms must be approximately π/ω), and operation with modulation frequencies below a few hundred Mc/sec becomes difficult since the path difference between the two beams becomes inconveniently large.

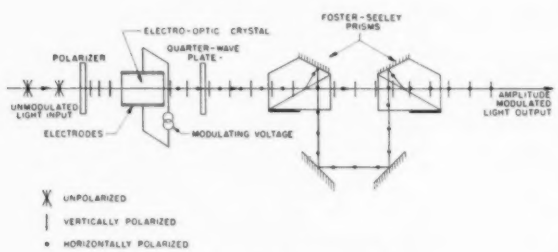

Fig. 1. Push-pull light modulator.

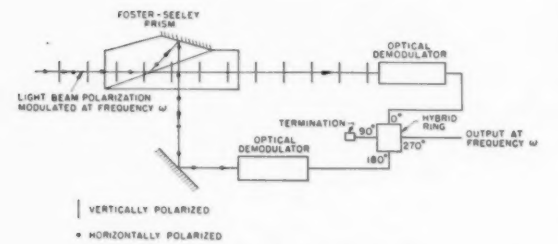

Fig. 2. Push-pull light demodulator.

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Intensity Distribution of Ruby Laser Beams

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Experiments concerning the stimulated optical radiation from rubies has been reported by many authors,[1-3] and it was pointed out that the angular divergence of the ruby laser beam is smaller than 1°.[4] However, the intensity distribution of the beam at larger angles has never been studied. For the investigation of scattering of laser beams from gases, the study of the intensity distribution of the beam and the nature of the side lobes associated with the direct beam are important.

In the experiments, two different ruby crystals described below were used:

1/ 6.35 cm long, 4 mm diam, doping 0.04% Cr, 90° orientation, ends flat within $\lambda/4$, parallelism 6 sec, dielectric coated.

2/ 6.35 cm long, 4 mm diam, doping 0.04% Cr, 90° orientation, one end flat within $\lambda/20$, total internal reflection type.

In the first laser configuration, the ruby placed at one of the foci of an elliptical mirror was pumped by a single flash tube (PEK XE 1-3) at the other focus of the mirror. The front end of the ruby was held by a holder in such a way that the beam emerged through a circular cylindrical hole 1 cm in diam and 4 cm in depth.

In the second laser configuration, the ruby was placed at the common focus of a double-elliptical mirror and was pumped by two flash tubes placed at the other foci. In this arrangement the front end of the ruby projected outside the laser box about 0.33 mm so that the light emitted from the ruby surface even at an angle of 90° was not obstructed by any ruby holder or by flash tube holders.

The study of the direct beam was carried out by directly exposing a 11 × 14 in. (28 × 35.6 cm) photographic film (Kodak RS pan) at 14.7 m from the ruby surface for a single shot. The photographs obtained by using the first laser configuration, for both rubies, are shown in Figs. 1 and 2. Due to the nonreflecting end of the ruby No. 2, a dark region through the center parallel to the plane of polarization is seen in Fig. 2. Unexpected intense side lobes parallel to the plane of polarization are observed for both rubies. Photographs similar to these were taken, using the second laser configuration, and no appreciable difference in pattern was observed. The photodensitometric curves (using Joyce Double Beam Microdensitometer Mark III) of the above photographs in the plane perpendicular to the plane of polarization are shown in Figs. 3 and 4 and that in the plane of polarization is shown in Fig. 5. In these figures the ordinate is calibrated in D units[5] and the abscissa in degrees of divergence of the beam.

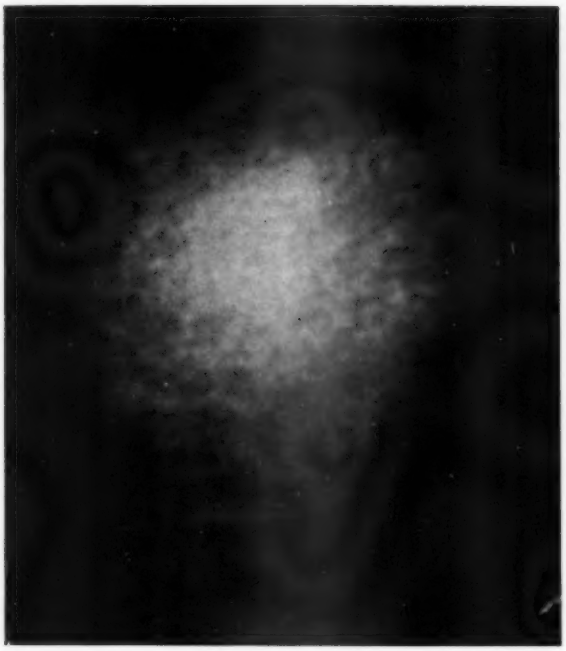


Fig. 1. The forward beam photographed at 14.7 m for the ruby No. 1 in the first laser configuration.

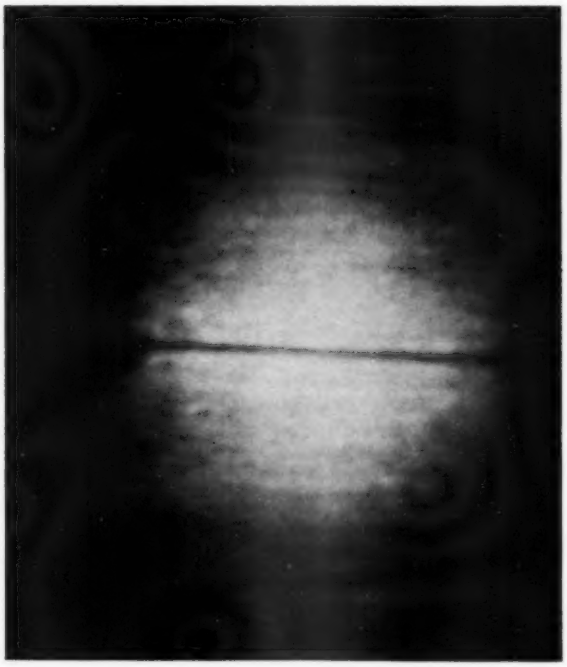


Fig. 2. The forward beam photographed at 14.7 m for the ruby No. 2 in the first laser configuration.

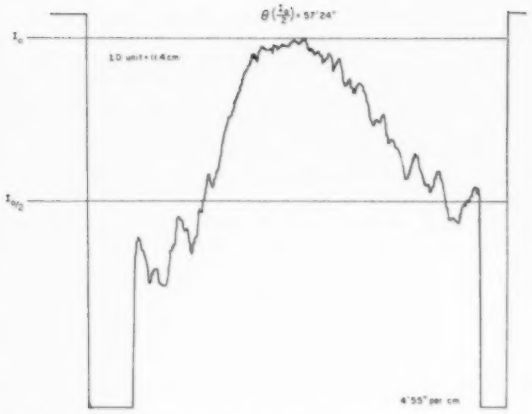


Fig. 3. The intensity variation of the forward beam for the ruby No. 1 in the first laser configuration in the plane perpendicular to the plane of polarization.

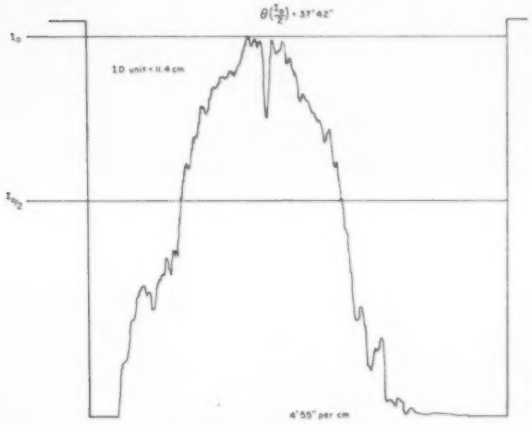


Fig. 4. The intensity variation of the forward beam for the ruby No. 2 in the first laser configuration in the plane perpendicular to the plane of polarization.

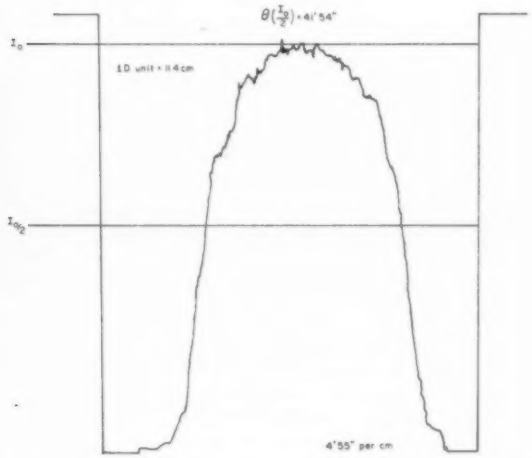
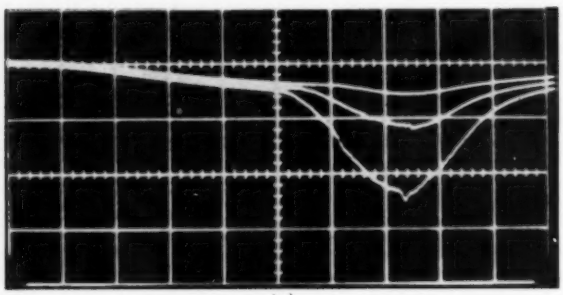


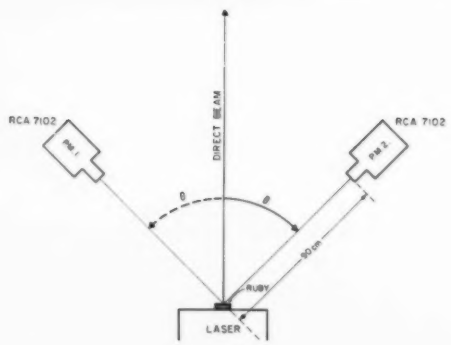
Fig. 5. The intensity variation of the forward beam for ruby No. 1 in the plane of polarization in the first laser configuration.

In each case the value of the angle, θ ($I_0/2$), corresponding to a reduction of the peak intensity, I_0, by a factor of 2 is given. The densitometric curves do not exhibit any sharp decrease in intensity with angular deviation in the direction perpendicular to the plane of polarization. But in the plane of polarization there is a sharp decrease in intensity with angle, as seen in Fig. 5, and in that direction there are no side lobes.

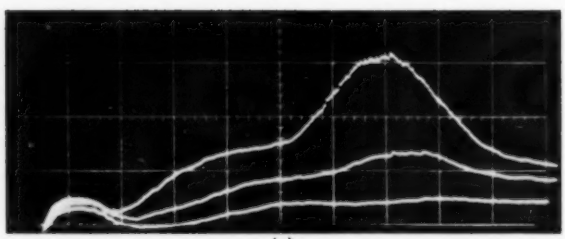
Since the photographic method was not sensitive enough for the range 0–90°, the study of the laser light distribution was carried out using photocells and photomultipliers. In the range 0–20°, an RCA 917 photocell, equipped with an interference filter centered at 6943 Å and a number of calibrated optical filters, were used. The interference filter was used to eliminate the flash light and the calibrated filters to attenuate the intensity of the incident light so that the photocell was operated in the linear region. The photocell was placed at various angles from 0–20°, and at each position the laser was operated at



(a)



(b)



(c)

Fig. 6. (a) Oscilloscope traces of photocell output at angle 10° with the main beam for laser voltages 1400 V, 1500 V, and 1600 V. Time scale: 100 μsec/div.; vertical scale 10 mV/div. (b) The experimental setup for the study of the intensity distribution of ruby laser beam. (c) Oscilloscope traces of the output of the differential amplifier when photomultipliers are placed at an angle 50° with main beam, for laser voltages 1400 V, 1500 V, and 1600 V. Time scale: 100 μsec/div.; vertical scale: 10 mV/div.

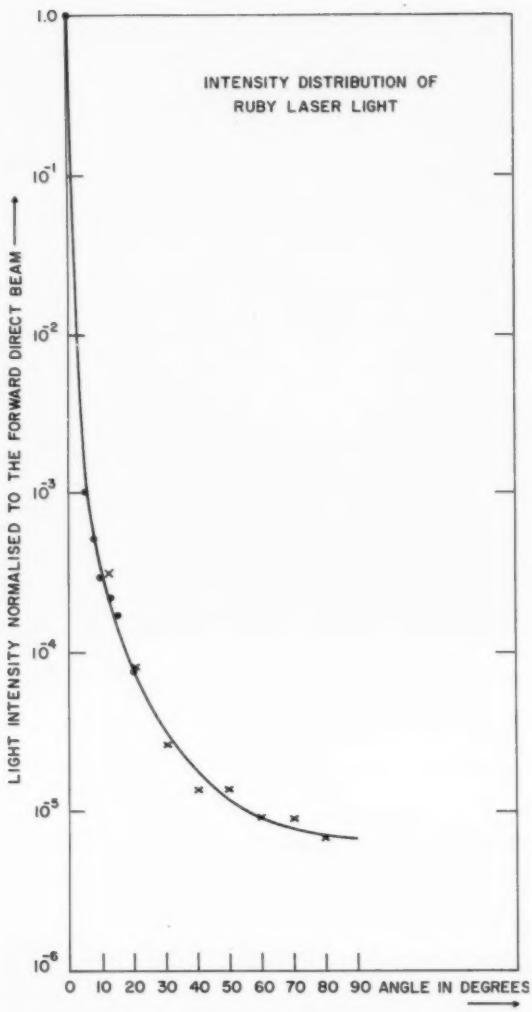


Fig. 7. The intensity distribution of the laser beam normalized to the intensity of the forward direct beam in the second laser configuration.

three different pumping voltages: (1) the threshold corresponding to 1400 V; (2) an intermediate level corresponding to 1500 V; (3) the level corresponding to 1600 V for which the results are obtained. (These pumping voltages correspond to 235 J, 270 J, and 307 J, respectively, of stored energy in the capacitors used to excite each flash tube.) In Fig. 6(a) the oscilloscope traces of the photocell output corresponding to these three voltages when it is placed at 10° with respect to the main beam are shown. The abrupt increase in the output at 500 μsec from the start of the flash light shows the beginning of laser action.

For the range 10–80°, the intensity of laser light is too small to be detected with the photocell and therefore two identical photomultipliers (RCA 7102) were used. The experimental setup is shown in Fig. 6(b). The ruby (No. 2) is placed in the laser so that the **E** vector is perpendicular to the plane in which the observations are made. The photomultiplier used in detecting the laser light [photomultiplier No. 2 in the Fig. 6(b)] is equipped with very narrow band interference filters centered

at 6943 Å and five red filters (Kodak 25) to ensure as little flash light and as much laser light as possible to be detected. In spite of such an arrangement the intensity of the flash light in the pass-band region of the system was found to be extremely large. Therefore a second identical photomultiplier (RCA 7102) was placed symmetrically with respect to the main beam and its output was used to cancel out the flash light contribution in the output of the other photomultiplier by subtracting one from the other in a differential amplifier. The compensating photomultiplier [No. 1 in Fig. 6(b)] was equipped with an interference filter centered around 6943 Å so as to detect light of almost the same spectral region from the xenon flash. If light from a different spectral region is detected by the compensating photomultiplier, the balancing of the flash light component may not be perfect. A blue filter (Corning 4-97) was used to cut down the laser light intensity and ensure linear response of the photomultipliers. The circuitry and the power supply voltage of the photomultiplier No. 2 were left undisturbed during the entire experiment, and the time constant of the circuit as well as the power supply voltage of the compensating photomultiplier were changed to obtain as perfect a balancing as possible when the laser was pumped just below the threshold. This was detected by displaying the output of the differential amplifier on an oscilloscope. The authors were forced to use rather large time constants to obtain a satisfactory compensation. This brought about the destruction of the spiky appearance of the laser output. After the compensation, the pumping was increased in steps as in the case of the photocell to 1400 V, 1500 V, and 1600 V. Figure 6(c) shows the oscilloscope traces at the angle 50° for all the three cases. The sudden increase in the output at 500 μsec is due to the lasering. The contribution due to laser light alone can thus be extracted from the photographs.

The curve obtained by the photocell (0–20°) and that obtained by the photomultipliers (10–80°) for the laser pumping voltage of 1600 V were matched for the range 10–20° by plotting them on semilog paper, and a continuous curve of the distribution of the laser light normalized to the intensity of the main beam was plotted against the angular deviation of the direction of observation from that of the forward beam. It is shown in Fig. 7. It is observed that the intensity of the observed light even at an angle 80° is reduced only by a factor of 10^8 from that of the forward beam. This most probably is due to the scattering of the laser beam by dielectric coating of the end surface of ruby crystal or crystal itself.

The authors wish to express their gratitude to L. Goldstein for his constant guidance and encouragement.

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Characterization of Bolometric Detectors

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In the course of determining many load curves for germanium bolometers operating at liquid helium temperatures, the author has found that extremely good approximations to load curve data can be obtained with the empirical relation,

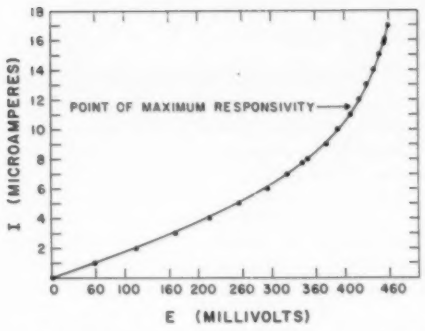

Fig. 1. Load curve for a typical germanium bolometer at T_c = 4.2°K.

$$R = R_0/[1 + (I/I_0)^n], \tag{1}$$

where R is the resistance of the bolometer element and I is the current through the element. R_0, I_0, and n are constants to be determined. Experimental data to support this observation are presented in Table I. Typical values of n obtained for germanium bolometers are 1.3 to 1.7.

Table I. Comparison of Measured and Calculated Load Curve Data for the Bolometer of Fig. 1

I (μA)	E (measured) (mV)	E (I, R_0, I_0, n) (mV)
10±0.1%	391±1%	391
11	408	407
12	420	420
13	430	431
14	440	440
15	447	447

From Jones' equations[1] and Eq. (1), it is possible to calculate the zero frequency responsivity and the value of the bolometer current which makes this responsivity a maximum. In addition, by making assumptions as to the resistance vs temperature variation for the detector material, one can also calculate the thermal conductance between the bolometer and its surroundings, as well as the temperature of the element at any operating current. With a knowledge of the thermal capacity of the bolometer element, it then becomes possible to calculate the bolometer time constant.

Procedure for Obtaining the Constants of Eq. (1). Once E vs I data (where E is the potential across the bolometer) for the bolometer have been taken (a typical load curve is shown in Fig. 1), R_0 may be determined from the data at very small currents.

If a plot of $[(R_0/R) - 1]$ vs I is then prepared on log–log paper, the points for bias currents of interest (i.e., those that are possible operating currents) will fall on a straight line. n is the slope of this line; I_0 is the current for which $[(R_0/R) - 1] = 1$.

Using this technique, it has been possible to fit load curve data to accuracies of better than 0.3% over the region of the curve where possible operating points exist.

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Sea Water Attenuation Measurements with a Ruby Laser

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Received 29 March 1963.

One of the uses frequently suggested for lasers is that of a source of radiation in underwater transmission. It is recognized that a laser having its radiation in the blue-green region of the spectrum is most desirable for such use because of the minimum attenuation coefficient in this region. However, it is of interest to determine how useful the present ruby-rod lasers might be in this application. Consideration was given to the underwater transmission ranges which might be attained; a range equation was derived and sample calculations were made. Because of the great spread in the existing attenuation data and the desire to avoid an interpolation in wavelength, a determination at the laser wavelength was performed for two sea water samples. One sample was obtained near shore at Point Mugu, California, and the other, four miles off shore near Long Beach, California. The samples were measured after a short period of storage.

The ruby laser used was a Raytheon Model LH-1 with a peak power output of 200 W (measured radiometrically). This laser has a 6.75 cm long by 6.3 mm diam corundum rod doped with 0.05% chromium. The rod, which has dielectric end coatings, and initiating flash tube are mounted at the opposite foci of a reflecting elliptical cylinder. The laser beam, after passing through a Wratten Type A filter, struck a beam splitter which diverted part of the beam to a silicon photodiode monitoring detector. The signal from this detector was displayed on an oscilloscope and photographed. The remainder of the laser beam passed through a small aperture into a tube containing the sea water sample and thence through standard Kodak gelatin neutral density filters onto an RCA 6199 photomultiplier. This signal was also displayed on an oscilloscope and photographed. Two sample tubes were used having lengths of 0.902 m and 0.155 m. The tubes were 3.2 cm in diam with blackened inner walls and optical-flat ends. The monitoring detector allowed the elimination of the effects of power variations in the laser pulses by always utilizing the ratio of photomultiplier to monitor signal. The attenuation coefficient was calculated by comparison of the signal ratios between the long and short tubes.

After the method was first checked with a sample of distilled water, the two sea water specimens indicated above were measured. Figure 1 shows the results together with measurements in in the visible region made or compiled previously by several workers.[1-6] Further information on light transmission in the sea is available in two articles by Duntley.[6,7] A very large spread in the values for any particular wavelength is evident; however, a rather smooth dependence on wavelength is seen for any given sample. The approximate upper and lower limits to the measured values are indicated in Fig. 1 by dashed lines. The laser-derived values appear to be in reasonable agreement with the older measurements.

The underwater range equation was derived assuming an exponential attenuation law and requiring a signal-to-noise ratio of 3. The result is

$$R(m) = -\frac{2.3}{\kappa}\log_{10}\left(\frac{3\ \mathrm{NEP}}{P}\right), \qquad (1)$$

where κ is the attenuation coefficient in m^{-1}, NEP is the noise-equivalent power of the detector in watts, and P is the laser power in watts. Factors such as multiple scattering, beam spread by diffraction, and collection efficiency were not included since only an approximate calculation was intended. As noted later, factors affecting the NEP will have only a small effect on the range. For a photomultiplier operating under optimum conditions (cooled cathode), an NEP of 10^{-16} W (6×10^{-14} lumens) has been reported.[8] This value, however, is for a 1.8 cps bandwidth and is thus too optimistic for a laser-detection system which requires a much greater bandwidth. It provides only a lower limit to the NEP. Utilizing the attenuation data of Fig. 1 and the value of 200 W for the Raytheon laser power, Eq. (1) yields the ranges shown in the upper part of Fig. 2. An upper and lower limit to the range is obtained by using the minimum and maximum values of the attenuation coefficient at the laser wavelength from Fig. 1. A range of 60 m can apparently be expected on the average.

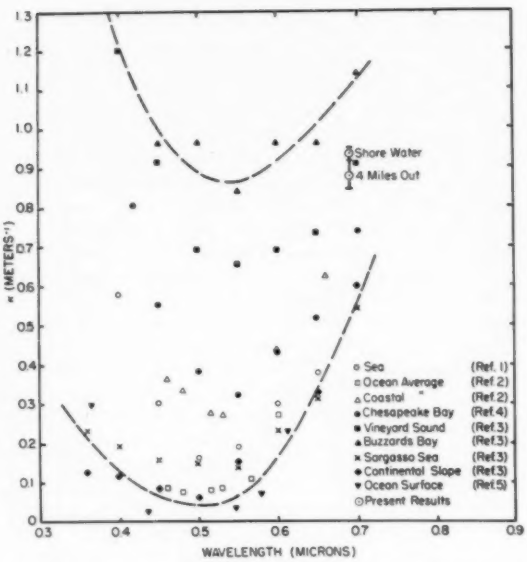

Fig. 1. Sea water attenuation coefficient κ as a function of wavelength in the visible. Present results shown by the dotted circles were measured with a ruby laser (0.6943 μ). Dashed curves give approximate upper and lower limits of κ.

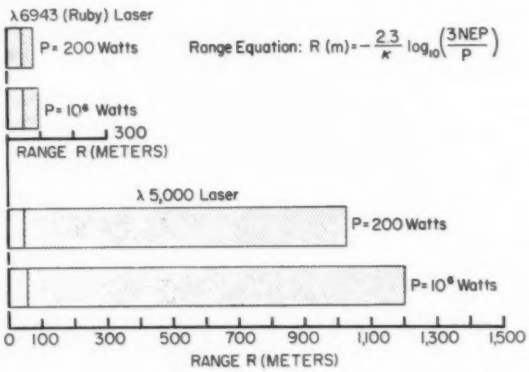
λ6943 (Ruby) Laser
P = 200 Watts
Range Equation: R (m) = -2.3/κ log10(3NEP/P)
P = 10⁶ Watts
300
RANGE R (METERS)
λ 5,000 Laser
P = 200 Watts
P = 10⁶ Watts
0 100 300 500 700 900 1,100 1,300 1,500
RANGE R (METERS)

Fig. 2. Calculated underwater range limits for ruby and hypothetical blue-green lasers. The longer and shorter bars indicate maximum and minimum ranges calculated using the extreme values of κ shown by the dashed lines in Fig. 1.

An attempt to estimate some possible ranges for other advanced lasers has also been made. The estimates are also presented in Fig. 2. Experimental lasers with powers in the megawatt range have already been reported.[9] With a ruby-rod laser of 1-MW power the range lies between 45 and 90 m. Lasers for the blue–green region are currently under development. Postulating a laser having 5000 Å radiation and a power similar to that of the Raytheon laser, the calculated range from Eq. (1) lies between 50 and 1000 m. A blue–green laser of 1-MW power will have a range of 60–1200 m.

Two significant points are evident from Eq. (1). First, reasonably large gains in laser power or decreases in detector NEP do not influence the range to a significant extent. For example, an increase in the laser's power by a factor of 10 or a decrease in detector NEP by the same factor will only give a range increase of about 5–10%. Second, the maximum range, especially for a blue–green laser, lies somewhere between very wide limits which in turn are due to the spread in values reported for the attenuation coefficient. Although some of this variation may be due to experimental error, most of it results from actual differences in the sea water in different locations.

From this brief study it can be concluded that ruby-rod lasers, even with high power levels, will have limited usefulness for underwater transmission applications. A blue–green laser would have a considerably greater potential in some underwater applications.

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A Continuously Variable Optical Beam Splitter and Intensity Controller

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Beam splitters and intensity controllers are required in optical instruments for experimental purposes and for communication. The partially silvered mirror which has been so widely used has the disadvantage that its reflectivity cannot be changed and that the absorption loss for the transmitted beam can be high. The purpose of this letter is to draw attention to the fact that well-known characteristics of total internal reflection lend themselves to this application.

Total reflection occurs when light strikes the interface of non-absorbing media from the optically denser side at angles of incidence exceeding the critical angle. Maxwell's theory predicts a penetration of the electromagnetic field into the rarer medium. The electric field intensity decreases with distance from the interface in an exponential manner, and the distance where the electric field amplitude is reduced to one-half of the amplitude at the surface is given by

$$x_{1/2} = \frac{0.693\lambda_D}{2\pi(\sin^2\theta - n_{21}^2)^{1/2}}.$$

Here, λ_D is the wavelength of the light in the denser medium, θ is the angle of incidence, and n_{21}, which is less than unity, is the relative index of refraction at the interface. The penetration depth vs angle of incidence calculated from this formula and for $n_{21} = 0.37$ is shown in Fig. 1(a). The depth of penetration is about $0.1\ \lambda_D$ at grazing incidence but reaches large values near the critical angle.

An important property of the penetrating field is that it is possible to couple to it and that the degree of coupling can be controlled continuously. It was recently shown that advantage could be taken of this property to measure film thickness and surface reliefs.[1] Schaefer and Gross,[2] and Hall[3] demonstrated this when they showed that the reflectivity of a totally reflecting prism could be continuously adjusted by adjusting the separation between two prisms in the range of zero to about

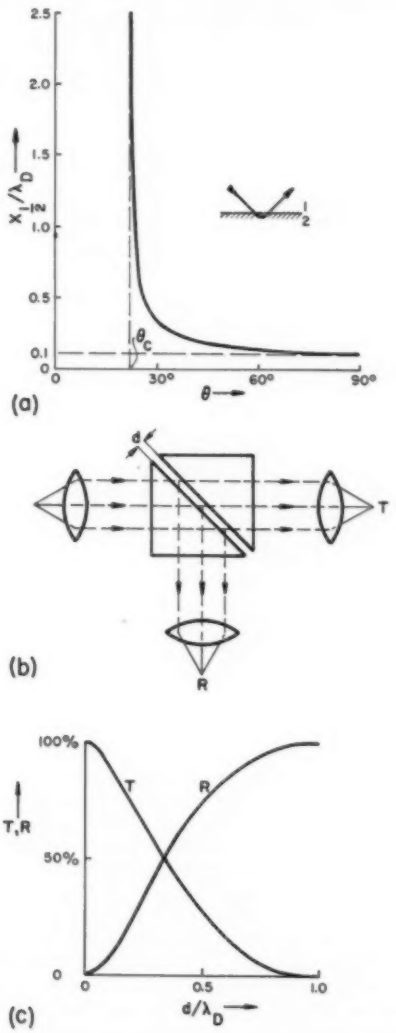

Fig. 1. (a) Penetration depth vs angle of incidence. (b) Means of coupling to penetrating field. (c) Transmission and reflection coefficients vs separation of the two prisms shown in Fig. 1(b).

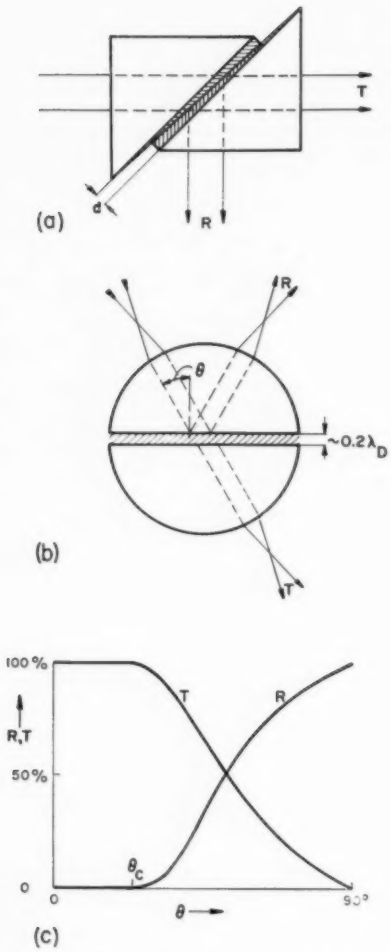

Fig. 2. (a) Degree of beam splitting accomplished by sliding one wedge relative to the other. (b) Degree of beam splitting accomplished by rotating the two hemicylinders, thus changing angle of incidence, hence penetration depth. (c) Transmission and reflection coefficients vs angle of incidence for beam splitter shown in Fig. 2(b).

one wavelength as shown in Fig. 1(b). Results obtained are shown [It should be realized that the degree of coupling can be slightly different for the different polarizations.[2,3] The use of the geometry shown in Fig. 1(b) as a double-prism attenuator for millimeter waves has also been demonstrated more recently[4]] in Fig. 1(c) where it is important to note that there is no loss at the interface where the beam is split, i.e., $T + R = 100\%$, neglecting reflectivity losses at the entrance and exit faces.

It is obviously possible to utilize this principle to make a continuously adjustable beam splitter and attenuator. The distance separating the prisms might be controlled mechanically. Another possibility is that two wedge-shaped films of lower refractive index than that of the prisms can be used. If the films are bonded to the prisms but not to each other, the distance separating the prisms, hence the degree of coupling, can be changed by sliding one prism on the other, as shown in Fig. 2(a). The performance of the beam splitter will be given by curves similar to those in Fig. 1(c). Since the penetration increases with increasing wavelength, the degree of coupling or the amount of transmission is wavelength dependent. This is no disadvantage for fixed wavelength sources such as optical masers but is a disadvantage for use in spectrometers. One can take advantage of this wavelength dependence to make a cold mirror by adjusting the separation between the prisms so that the rays of longer wavelength (heat waves) are substantially transmitted while the shorter visible rays are reflected.

The angular dependence of the penetration suggests still another means, shown in Fig. 2(b), of constructing the variable beam splitter. By choosing a fixed distance between the hemicylinders, the degree of coupling can now be adjusted by rotating the complete assembly. Its performance is shown in Fig. 2(c). The hemicylinders should be large compared to the beam width so that the light rays in the beam can be maintained substantially parallel within the beam splitter. The transmitted beam emerges essentially undeviated with respect to the incoming beam. Unlike the previous construction, the reflected beam will deviate since the angle of incidence changes. This device can be made by optically contacting the two flat surfaces after the desired thickness of insulating layer of lower index has been evaporated on one of the two surfaces. (Optical contact can be easily achieved between two surfaces polished flat to within 1/20 λ of sodium light.)

A laboratory model of a beam splitter of the type shown in Fig. 2(b) was constructed and qualitative results demonstrating its feasibility were obtained. The hemicylinders were made from quartz where the flatness of the inner surfaces was less than that required for optical contact to occur. Thus, when the hemicylinders were placed together a film of air of nonuniform thickness separated them, where it was possible to decrease the thickness of this film by increasing the pressure of one hemicylinder against the other. If too much pressure was applied, the surfaces became distorted and optical contact occurred, making the inner surface perfectly transparent for all angles of incidence. When an air space was present between the flat surfaces, the device was found to operate for both the transmitted and reflected light in the manner shown by the curves of Fig. 2(c) for wavelength range tested from the visible out to 3.5 μ. The degree of coupling to the penetrating field was found to increase as the wavelength increased and as the space separating the two hemicylinders was decreased.

The techniques discussed here can be used for electromagnetic waves from the visible right out to the microwave region.

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Variation of Lead Sulfide Response with Incident Angle and Orientation in Detector Plane

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The response of lead sulfide photoconductors as a function of both the angle of incidence of the radiation and the orientation of the detector in its own plane was recently measured at these

laboratories. The results were generally in agreement with those reported by Schaefer[1] as to the deviation from cosine response. Additionally, at a fixed incident angle a variation in effective responsivity was noted as the detector was rotated in its own plane. The samples tested were a selection of commercially available cells from different manufacturers. They were all of approximately the same shape and physical construction.

The experimental setup and cell geometry are shown in Fig. 1. Figure 2 shows the normalized response for two different orientations for an Eastman Kodak Ektron detector type N. Similar results were obtained for the other cells included in the experiment. These were: Kodak Ektron type O, Kodak Ektron type P, Kodak Ektron type Q, Infrared Industries type B1, Infrared Industries type B3, and Bulova type J.

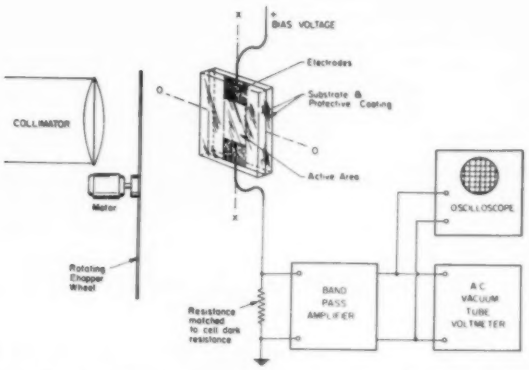

Fig. 1. Experimental arrangement and cell construction.

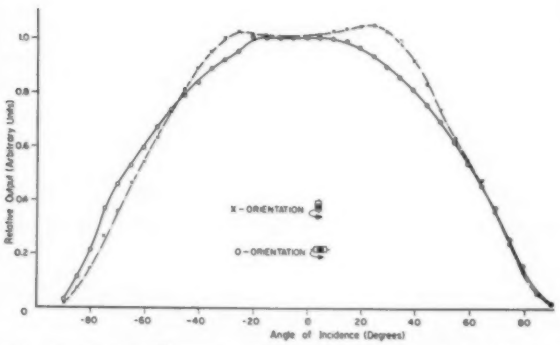

Fig. 2. Relative response of PbS detector as a function of angle of incidence. (Orientation of detector in its plane is the parameter.)

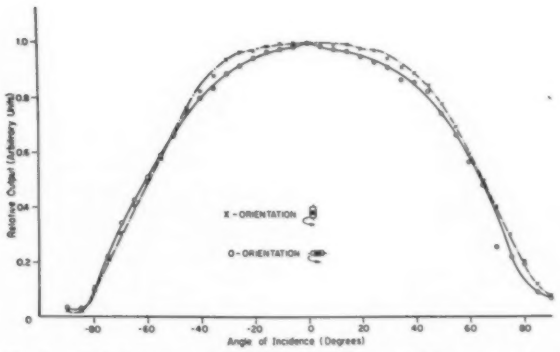

Fig. 3. Relative response of PbS detector with blackened edges as a function of angle of incidence. (Orientation of detector in its plane is the parameter.)

An explanation of this effect was implied in ref. (1). The PbS detector is a sandwich construction with the active material between a transparent substrate and a protective covering. At oblique angles some light enters the substrate through an edge or an uncovered surface. The amount of light that enters, for a given incident angle, depends upon the orientation of the detector in its plane. Internal reflection within the substrate or covering causes this stray radiation to be absorbed by the PbS.

Since two of the edges are adjacent to the electrodes, the response to radiation at a given angle of incidence is not uniform as the detector is rotated about an axis normal to its surface. The response is a function of the geometry and optical parameters of the particular cell.

Confirmation of this explanation was obtained by masking all but the active area. Figure 3 shows these results.

The measurements are of interest since detectors of this type are often used to define an optical field of view based on the dimensions of the active area.

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He–Ne Laser as Source for Light Scattering Measurements

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Received 19 July 1963.

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The purpose of this Letter is to compare the qualities of the continuous He–Ne laser as a monochromatic source for light scattering studies relative to conventional sources such as a bright line from the spectrum of a mercury arc lamp. In this study, the scattering of the $\lambda = 6328$ Å beam of a continuous He–Ne laser such as described by Herriott[1] was compared with the scattering of the strong line $\lambda = 5461$ Å of an 80-W Hg arc source. The scattering was produced by spherical polystyrene latex particles in water. The latex sizes were determined by electron microscopy and supplied by Vanderhoff.[2]

Figure 1 shows the source intensity distribution from the laser, the scattering curve of a 2 mm thick sample of water, and two curves I_1 and I_2 showing the scattering from a 2 mm thick sample of 10^{-3} volume concentration of 2.89 μ diam polystyrene latexes in water. The curves for I_1 and I_2 refer to the incident electric field vector **E** of the polarized laser beam perpendicular and parallel to the scattering plane.

Figure 2 shows the source intensity distribution of the filtered (Kodak-Wratten filter #77) $\lambda = 5461$ Å line of the Hg lamp, the scattering curve from a 1 mm thick sample of water, and the scattering curve from a 1 mm thick sample of 10^{-3} volume concentration of 2.89 μ diam polystyrene latex particles for the randomly polarized incident beam.

Figure 3 shows an attempt to compare the scattering data with the well-known Mie[3] theory for the light scattering from spherical particles. According to the Mie theory there are only two important parameters of the scattering: m, the relative index of refraction of the scattering sphere to the index of refraction of the external medium, and $\alpha \equiv \pi D/\lambda'$, or π times the diameter of the particle divided by the wavelength of the incident radiation in

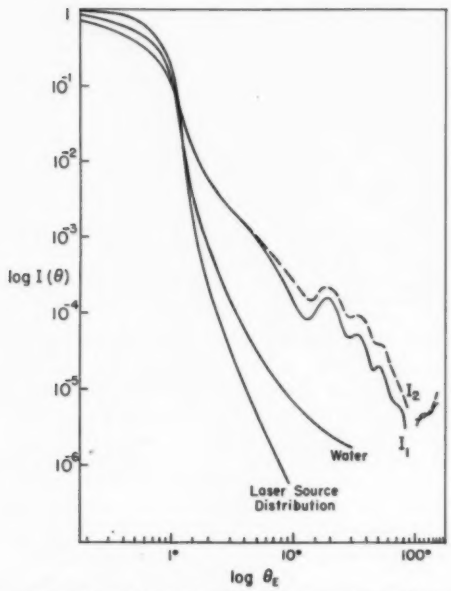

Fig. 1. Log-scattered intensity $I(\theta)$ vs log experimental scattering angle θ_E using laser source.

the external medium. A good review of this light scattering theory has been given by van de Hulst.[4]

In the case of light scattering from polystyrene latex spheres in water, the Mie theory scattering angle θ differs from the experimental scattering angle θ_E by

$$\sin\theta = \frac{\sin\theta_E}{n_w} = \frac{\sin\theta_E}{1.333},$$

where n_w is the index of refraction of water. Also, the Mie theory parameter α becomes

$$\alpha = \frac{n_w \pi D}{\lambda},$$

where λ is the source wavelength in air. The curves in Fig. 3 are plotted vs the Mie scattering angle θ.

Five curves are plotted in Fig. 3, showing details of the scattered intensity in the range of scattering angle $\theta < 30°$. Table I presents a summary of the data pertaining to the five curves in Fig. 3.

Table I. Data for Five Curves in Fig. 3.

Curve	Particle diameter	Source	Wavelength (Å)	m	α
1	2.89 μ	Hg	5461	1.202	22.2
2	Mie	theory	—	1.20	20.0
3	2.89 μ	Laser	6328	1.197	19.2
4	2.12 μ	Hg	5461	1.202	16.5
5	Mie	theory	—	1.20	15.0

All the curves in Fig. 3 are plotted at an arbitrary intensity relative to each other. Curves 1 and 4 show the scattering data using the Hg source. Curves 2 and 5 give the calculated intensity $I(\theta)$ from the Mie theory for $m = 1.20$, $\alpha = 20$, and $\alpha = 15$. Curves 2 and 5 were calculated using the coefficients of Chu *et al.*[5] Curve 3 shows the laser data plotted in the form $I(\theta) = {}^1/_2 (I_1 + I_2)$, which is equivalent to the randomly polarized incident light case according to the theory.

Thus, Fig. 3 indicates how the first intensity minima and maxima of the scattered light vary with α. Comparison of the experimental positions of intensity minima and maxima with theory is often used to determine particle sizes. From the curves in Fig. 3, the light scattering experimental values for the particle sizes appear to be slightly less than the values given by Vanderhoff. Also, in Fig. 3, it is evident that the experimental curves do not show quite as much fluctuation in intensity as the theoretical curves indicate. This is partly due to the fact that these data are for a large number of scattering particles in a large volume, whereas the theory gives the scattering distribution of a single

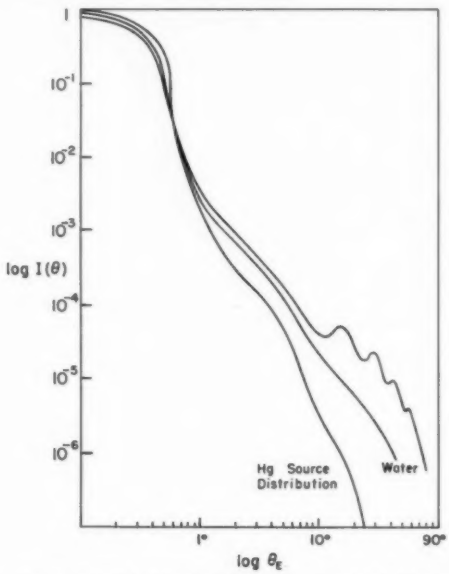

Fig. 2. Log-scattered intensity $I(\theta)$ vs log experimental scattering angle θ_E, using Hg source.

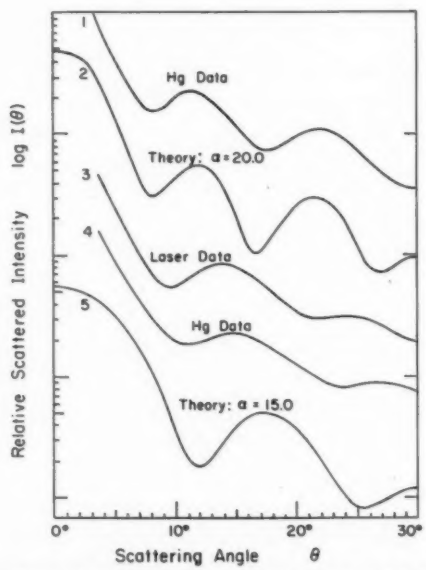

Fig. 3. Comparison of single light scattering data with Mie theory

particle. Also, since rather high volume concentrations of particles are used, there is some multiple scattering.

The major advantage of the laser for light scattering studies is that it is easy to make measurements at any angle θ from forward scattering at $\theta \approx 0°$ to backscattering at $\theta \approx 180°$. The measurement of backscattering with conventional sources is difficult because beam-defining apparatus usually gets in the way. Since the laser beam is well defined, there is no need for the many apertures and beam-defining slits such as are used with the Hg source. Usually, the defining slits for conventional source beams give messy diffraction effects in the source distribution, such as is evident in Fig. 2.

The source intensity of the laser beam at $\theta = 0°$ is about the same as the intensity for the 80-W Hg lamp $\lambda = 5461$ Å line. However, when using a polarizer with the Hg source to make scattering measurements of I_1 and I_2, the polarized incident intensity obtainable from the laser is higher. With the laser, it is necessary to use a filter at the exit port to get rid of the continuous diffuse light coming out the end. It is best to work at some distance from the end of the laser to minimize the diffuse light background.

The author wishes to thank D. Hewitt and F. Barnes of the University of Colorado, Dept. of Electrical Engineering, for providing the use of the laser.

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Microdensitometer Modification for Continuously Scanning Angularly Oriented Spectral Lines

Alwyn F. Wiebe

Barnes Engineering Company, Stamford, Connecticut.
Received 13 June 1963.

Most laboratory spectrographs are designed and operated with slits that are parallel to the diffraction grating rulings or prism apex. This is necessary to produce spectral lines perpendicular to the axis of dispersion. However, when objective spectrographs are used to photograph rapidly moving point sources such as meteors, it is difficult to assure parallelism of the grating rulings or prism apex and the source motion. As a result, the spectral lines are often imaged at an angle to the axis of dispersion.

When spectrograms are analyzed, measurement of the photographic density of the lines is of importance. An instrument frequently used for such measurements is a traveling carriage microdensitometer. It is necessary on many commercial microdensitometers that the spectral lines and axis of dispersion be perpendicular, or nearly so, for no adjustments are provided to rotate the scanning slit to accommodate angularly oriented lines. The operator is thus forced to scan the spectrum in segments rather than continuously. This increases the operating time and probability of inaccurate measurement of densities.

A simple, inexpensive, optical device was incorporated in a Jarrell-Ash Model 2305 microdensitometer to make it possible for such spectra to be scanned conveniently and continuously. A dove, or inverting prism, was placed in the long conjugate of the projection lens, see Fig. 1, and when rotated about the optical axis the projected image of the spectrum was correspondingly rotated. Thus, the axis of dispersion remains parallel to the carriage motion while the spectral lines can be optically rotated until parallel to the stationary scanning slit.

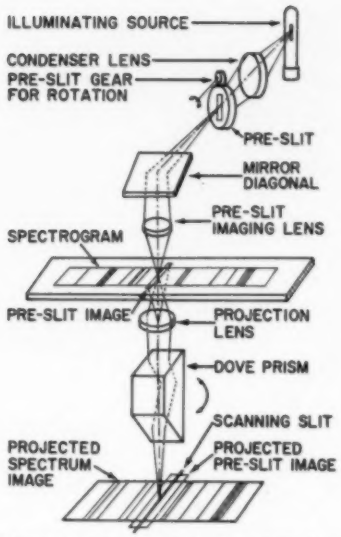

Fig. 1. Functional diagram of optical system for continuously scanning angularly oriented spectral lines.

As the preslit is imaged on the spectrogram and is fixed so that its projected image is superimposed on the scanning slit, any optical rotation of the projected image of the spectrum also rotates the preslit image. This is compensated for by rotating the preslit sufficiently in the opposite direction, until its image is superimposed on the scanning slit as designed. This was accomplished by gearing the preslit mount to an external shaft within reach of the operator.

With the above arrangement, spectra with lines oriented as much as 45° from the axis of dispersion have been scanned without difficulty. The slight change of optical path created by the prism slightly reduced the image magnification but this is of slight consequence. Additionally, a slight loss of instrument sensitivity was observed but was not significant.

It should be observed that the prism was not operated in strictly collimated light but the small angles subtended by the preslit and spectral lines nearly approximated paraxial conditions, and the prism did not significantly contribute to image degradation.

Spectroradiometry by Means of Modified Spectrophotometers

Harry K. Hammond, III

National Bureau of Standards, Washington, D.C.
Received 25 June 1963.

Spectroradiometric data on light sources have been obtained in relatively small quantities by relatively few laboratories with a variety of equipment designed or assembled locally for this explicit purpose. The author knows only one instrument of American manufacture that was marketed as a spectroradiometer for light sources, and it is no longer available. The small number of instruments required per year and the specialized use discourage instrument manufacturers from attempting to design spectro-

radiometers. The requirements for this type of instrumentation are conveniently met by modification of spectrophotometers designed for reflectance and transmittance measurements. Two papers reporting such modifications have appeared recently in *Applied Optics*. Brown[1] describes the modification of a General Electric (GE) recording spectrophotometer. Grum[2] describes a modified Beckman DK-2R recording spectrophotometer. These papers are welcome additions to the instrumentation literature, but like other recent papers on spectroradiometry they fail to deal with the evaluation of the intensity of spectral lines and tend to mislead the reader to conclude that accurate spectroradiometry of complex light sources is much more simple than is actually the case.

There is no disputing the fact that spectrophotometers can be modified to draw a curve that resembles the spectral irradiance distribution one would expect to obtain from a source such as a fluorescent lamp. Difficulties arise, however, when one asks such questions as: What does this curve mean? What is the irradiance from each of the various mercury lines relative to that from the continuum at the corresponding wavelengths? These are not new questions, but the papers cited above fail to discuss these important points. The GE spectrophotometer is designed with cams to provide an approximately constant passband. The Beckman spectrophotometer, however, is designed to adjust the slits automatically while scanning the spectrum so as to provide constant photomultiplier signals for the reference beam. This means that the slit width, and thus the passband, is a function of the spectral irradiance from the reference source. This method of operation is acceptable in spectrophotometry, where the light source, which is part of the instrument, emits a continuum and where the spectral curves are similarly continuous. Accurate spectroradiometry of sources containing spectrum lines, however, requires an accurate evaluation of the passband at the wavelength of the line. Accurate evaluation is more difficult when the passband is a function of the irradiance from the standard. For this reason constant mechanical slit widths are often preferred in spectroradiometry even in the case of prism instruments.

One purpose of this Letter is to suggest that each experimenter record slit settings and include the passband of the monochromator when reporting spectroradiometric data. The problem of accurately assessing the intensities of spectral lines relative to continua is not an easy one, and a full discussion is beyond the scope of this Letter. Lord[3] discussed the problem from a theoretical point of view; Jerome[4] and Henderson and Hallstead[5] discussed this problem and others from the experimental point of view. Suffice it to say here that each experimenter must tackle the problem and that the accuracy of his solution should be verified experimentally by taking data with widely different slit settings. Furthermore, he should not be content to apply without verification the dispersion curve of the instrument supplied by the manufacturer. Different slit configurations for double monochromators are advocated by various experimenters. In the one most frequently used by the author, the entrance and exit slits are set equal and the middle slit is set for a greater width. Under these conditions the recording of the line intensity is essentially triangular, and the intensity is proportional to the area and is computed from the product of the measured height of the line above the continuum and the width at half height. The width must be evaluated accurately, ideally on an expanded wavelength scale. When integration is required as in the determination of luminous flux or chromaticity coordinates, it is customary to obtain an equivalent intensity of the line by dividing the area of the triangle computed above by the integration bandwidth, usually 10 nm. If the lines are sufficiently spaced or the dispersion sufficiently high so that all lines are completely resolved, there is no great problem in their evaluation. The difficulty arises in the case of high-pressure arcs such as mercury and xenon when lines are broad and overlap. Here again, the simplest solution appears to be to take data with equal entrance and exit slits and then to use a very fine integration bandwidth, say 1 nm, and simply treat the lines like rapidly varying continua.

Most experimenters have realized that the solid angle subtended at the entrance slit by the collimator lens or mirror of the spectroradiometer must be filled with light from the test lamp and from the standard lamp in turn. To fill the collimator, a diffuser is frequently employed. At first thought, any diffuser, reflecting or transmitting, would seem to be satisfactory. Transmitting diffusers appear to offer an advantage because they can be made to pass a maximum of flux in the near rectilinear direction. However, experimenters who have made careful measurements with transmitting diffusers of ground glass or quartz have discovered that the tiny prismatic facets of these diffusers can cause systematic error. When a ground glass diffuser is irradiated by a lamp of known color temperature, the light transmitted by the diffuser in a rectilinear direction has a lower color temperature. This reduction in color temperature is caused by the fact that, in the process of transmission through the diffuser, blue light is preferentially deviated from the rectilinear direction to a larger extent than is red light. This phenomenon is caused in ground diffusers by the dispersion of the prism facets. In opal glass it is due to the fact that the opacifying particles are of the same order of size as the wavelength of the light.

Middleton and Smith[6] made an extensive investigation of the diffusion of light by ground glass. Their data show that for crown glass and perpendicularly incident incandescent-lamp light of color temperature 2850°K, the light transmitted in the rectilinear direction is lowered in color temperature by a minimum of 150°K for a coarse-ground surface to a maximum of 550°K for the finest grind investigated. With the finest grind and an angle of view above 45°, the color temperature was raised by as much as 150°K. If the same diffuser is used with standard and test lamps, this effective change in color temperature, really a change in spectral distribution of the transmitted light, is not important as long as the two sources subtend the same angle at the diffuser. When a tubular fluorescent lamp, or even a short section of such a lamp, is measured relative to an incandescent lamp, ground glass diffusers should be avoided because of the spectral distribution error introduced by them with the change in angle of the source subtended at the diffuser. Reflecting diffusers are therefore preferred for comparing sources of different areas or geometric distribution of emitted flux. Plane surfaces of any diffusing material may be used, but the use of a small hollow sphere, with suitable openings, coated on the inside with a highly diffusing material (such as barium sulfate for the visible spectrum) has the great advantage of providing a mixing mechanism, thereby permitting the diffuser to be irradiated from one direction by a nonhomogeneous beam and viewed by the monochromator from another direction, usually at right angles to that from which the sphere is irradiated, without any spatial inhomogeneity. If it is desired to compare two sources wavelength by wavelength, the sphere can be mounted so that it can be rotated about the viewing direction and the two sources can be mounted so that their irradiating directions make 90 degrees with the viewing direction and 90 or 180 degrees with each other.

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OSA Around-the-World Group Flight 1964

Revised Information # 2

The International Commission for Optics' Symposium on Photographic and Spectrographic Optics will be held in Tokyo 1–8 September 1964, preceded by a Conference on Interference and Coherence, convened under the auspices of ICO and the Australian Academy of Science, in Sydney 23–29 August 1964. The airlines have recently approved an around-the-world group flight fare for 15 persons or more, and OSA now wishes to learn the number of members who are interested in attending these two meetings and participating in this group flight. There will also be an informal universities tour in Israel and in Hong Kong, and time for sightseeing in New Delhi, Bangkok, and Teheran. Our revised schedule now looks like:

Aug.	8	leave New York, Idlewild Airport
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	13	Teheran
	14–17	New Delhi
	17–20	Bangkok
	20–22	Hong Kong
	23–31	Sydney, ICO meeting
Sept.	1–10	Tokyo, ICO meeting
	10	return to NYC via San Francisco*

The group fare will be **$1475** economy class round trip. Only OSA members and their immediate dependents may participate. Would members who are interested fill in and return the form below. The interest of those who have already written in is recorded, **and a $100 deposit is now needed.** Please send in your deposits as soon as possible. Deposits, less 10% handling charge, will be returned in the event of cancellation before 1 June 1964.

See also page, A12

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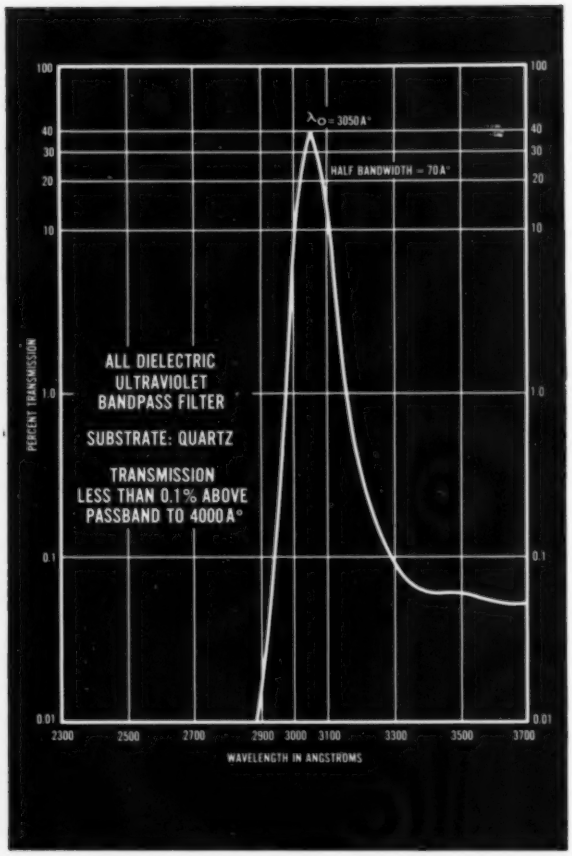

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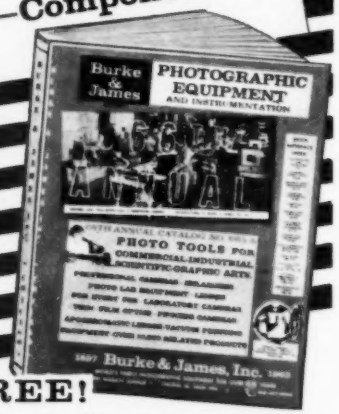

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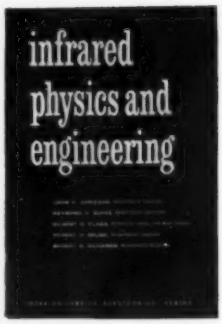

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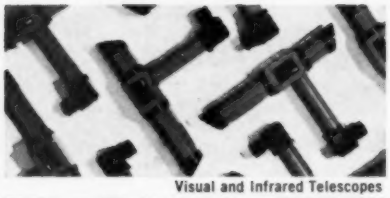
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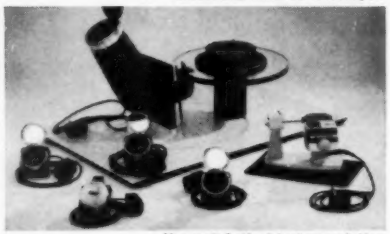
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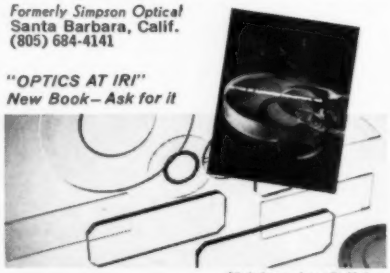
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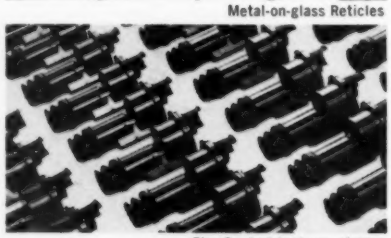
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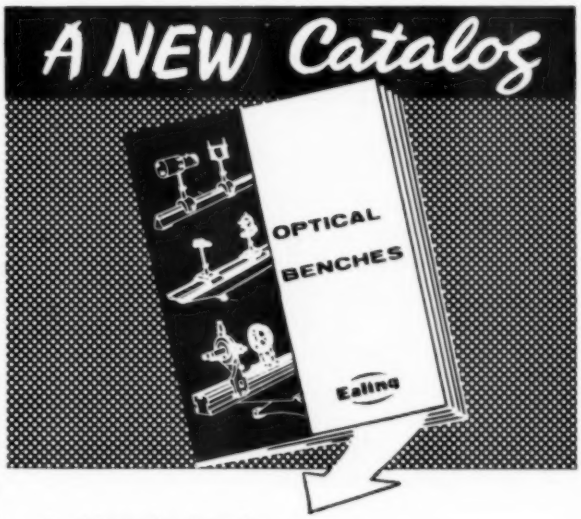

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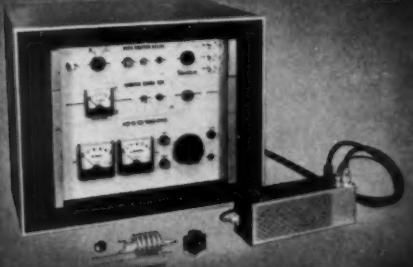

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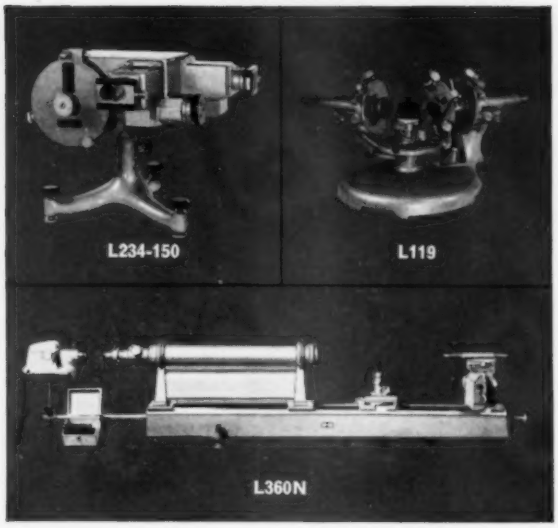

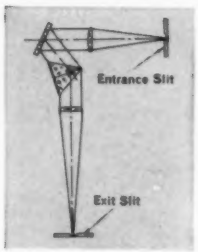

Optical Diagram of
L234-150 Monochromator

DEPENDABLE ACCURACY

Gaertner Scientific thrives on solving difficult measuring problems . . . with precision unexcelled—reputation unsurpassed. Instruments shown represent a few of the many optical measuring systems available that can be applied or modified to your requirements.

L234-150 QUARTZ MONOCHROMATOR—High speed enables studies of absorption spectra, photosensitive materials, phosphorescence, and energy distribution. With camera attachment, unit converts to high aperature spectrograph. **Request Bulletin 158-61**

L119 ELLIPSOMETER—Accurate measurement of extremely thin film down to 2 or 3 Angstroms. Also adaptable to birefringence and surface studies with elliptically polarized light. **Request Bulletin 203-61**

L360N OPTICAL-INSTRUMENT BENCH—For checking optics, experimental and mock-up arrangements requiring alignment, unique positioning, linear or rotational movement of test pieces or components. **Request Bulletin 156-59**

Your inquiry for existing or proposed instrumentations will be answered immediately. GSC-3-219

Gaertner
SCIENTIFIC CORPORATION
1294 Wrightwood Ave., Chicago 14, Ill.
Area Code 312, BUckingham 1-5335

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40th ANNIVERSARY

Steady growth during the past 40 years, finds us today with an extremely wide variety of essentials that meet the exacting requirements of modern technology.

Our plant, which covers over 20,000 square feet, is producing an ever increasing number of products for both science and industry. It includes an optical division with unsurpassed facilities for grinding, polishing and surfacing, an instrument shop with modern machinery, a high-vacuum coating laboratory as well as a section for the manufacture of diamond-impregnated tools using a sintering process for metal matrix only for working of quartz, glass, ceramics or other hard, brittle material. We also import and distribute the finest optical glass. We'll be glad to study your requirements and give you our recommendations.

MULTI-LAYER INTERFERENCE FILMS

Made in our New Rochelle High Vacuum Coating Laboratory

For dichroic and achromatic beam splitters and filters. High efficiency. . .Relatively wide band

Our coatings were used in the first TELSTAR color TV transmission

For lasers and masers

Over 99% reflectivity

#530–630	reflects 530 mμ to 660 mμ
#N-6343	reflects 610 mμ to 710 mμ
#N-680	reflects 670 mμ to 750 mμ
#N-1064	reflects 980 mμ to 1120 mμ
#N-1150	reflects 1120 mμ to 1220 mμ

Coatings are also available with peak reflectivity at any other desired wavelength.

Unaffected by immersion in liquid nitrogen. Can easily be cleaned with Acetone, Alcohol, or normal detergents.

ABSORPTION TYPE COLORED OPTICAL FILTER GLASS

Processed in our New Rochelle Optical Shop in about 100 types for the ultra-violet (from 250 mμ), visible, and infrared (to 3000 mμ) spectral regions. Available in flat or as solid bars for the manufacture of tubing for liquid laser excitation.

Also Anti-Laser Eye-Protection Filter Glass BG-18

●

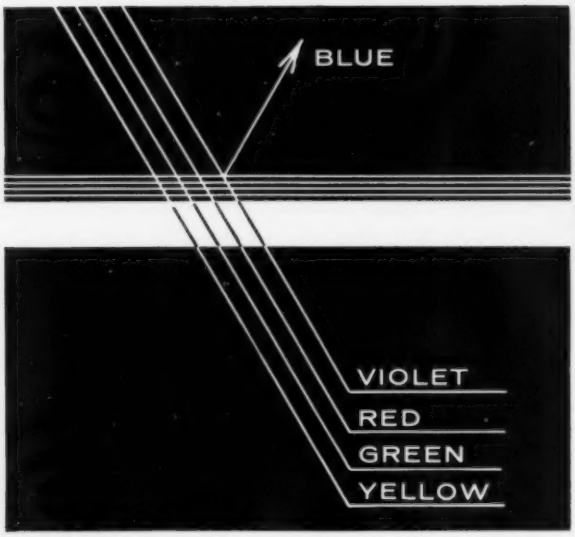
NEODYMIUM DOPED GLASSES FOR SOLID STATE LASERS

Type	LG-2	LG-4
Basic Glass	Borosilicate glass	Lanthanum-Borosilicate glass
Doping	2 weight % Nd_2O_3	2 weight % Nd_2O_3

Emission wavelength: 1.06 μ

FISH-SCHURMAN CORPORATION
90 Portman Road, New Rochelle, N. Y.

WAVE LENGTHS, TO ORDER



Multilayer vacuum-deposited coatings can put light to work in several ways

These coatings, applied in separate layers to glass or plastic, allow you to split light beams in many ways on a single application. Multilayer coatings can be applied to produce a specific beam-splitting result.

Liberty Mirror engineers can do all the design and development work on any potential use for this technique, or help solve application problems.

Vacuum-deposited coatings of various metals are used to make front-surface mirrors, neutral filters, transparent mirrors, high-efficiency beam splitters, beam-splitting dichroic mirrors and filters. Metallic and transparent electrically conducting coatings are available for resistance heating. Static-dissipating and high-frequency shielding coatings are also available.

Applied to all types of glass, metal or plastic, the coatings are used in such varied products as scientific and optical instruments, cameras, toys, pin setters, wheel-aligning equipment, aircraft and missiles. Free data sheets are available on all coatings.

Write L·O·F, Liberty Mirror Division, 55113 Libbey·Owens·Ford Building, Toledo 2, Ohio.

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MADE IN U.S.A.
LOF GLASS

MELLER CRYSTALS

Wherever your laser research program is pointing . . . communications, medicine, metallurgy, weaponry . . . Meller's tremendous inventory of stock single crystals is available to supply your laser needs instantly.

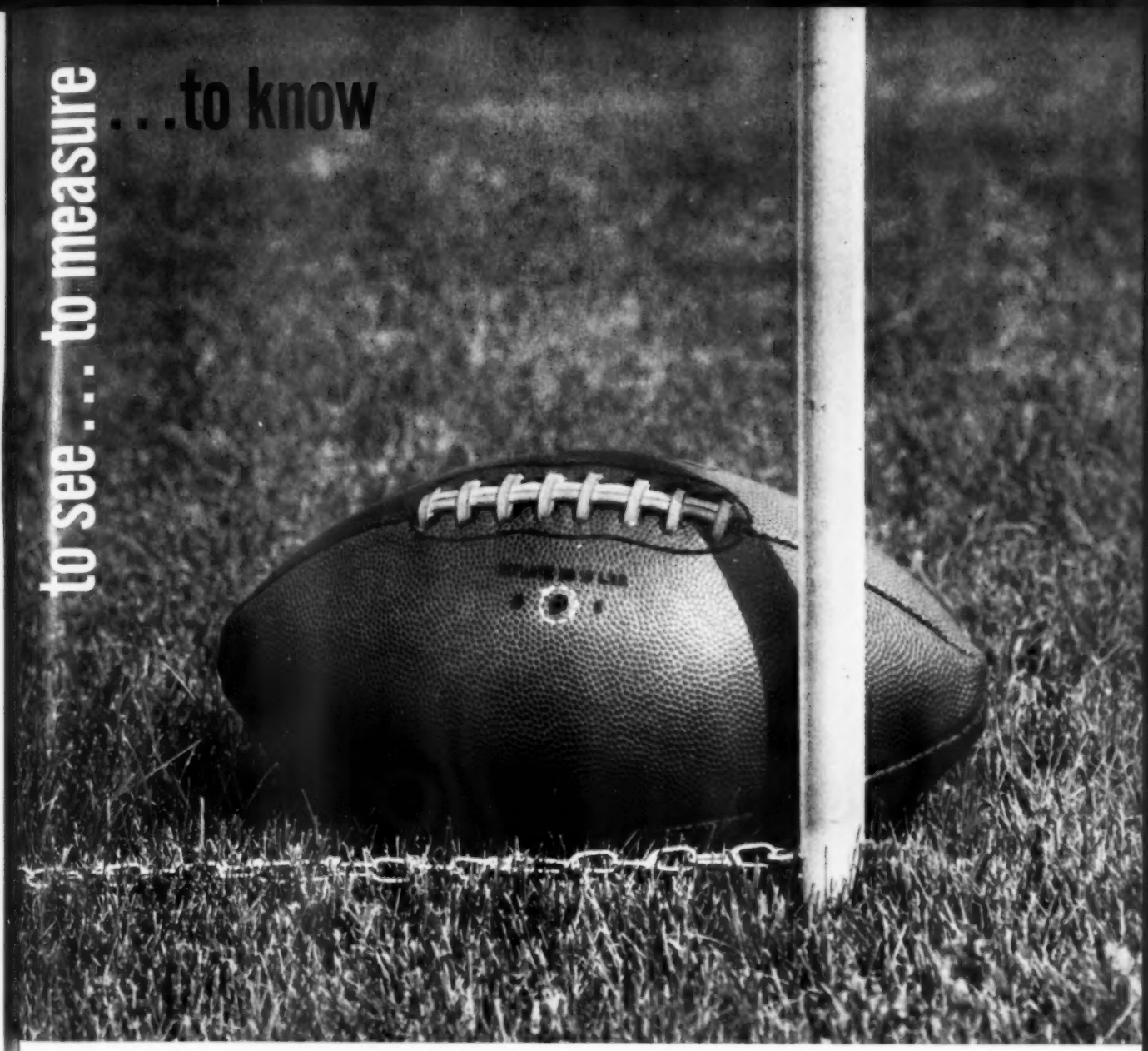
All configurations: plain flat and parallel ends, TIR, Brewster's angle.

All types: Ruby rods to 12" □ 2% neodymium doped super-quality glass □ .5% neodymium doped calcium tungstate to 5" □ .1% samarium or .5% neodymium doped strontium fluoride □ .5% neodymium or .1% uranium doped barium fluoride □ calcium fluoride doped with .5% neodymium or .1% samarium or .05% dysprosium (up to 6") or .1% uranium.

For current stock lists and prices, write or call Adolf Meller Company, Box 6001, Providence, Rhode Island. (Phone 401-331-3717)

MELLER

Synthetic Sapphires • Laser Crystals • Alumina Powders



First down?

Two stakes and a chain tell the story — a simple but surprisingly accurate measuring device. The more accurately it measures, the less in doubt the outcome. Both here and where the stakes run higher — in industrial efforts, in the conquest of space — to measure is to know.

The more precise the measurement, the more you know. Narrowing the meaning of precision, toward the end of broadening man's knowledge, is the special function and talent of the Optics & Metrology Division at K&E.

K&E welcomes your inquiries on problems along the following lines — at any stage.

Space and Missiles Systems

Solar and Star Simulators ● Cine and Special Theodolites ● Antenna Contour Checking Instruments ● Contour Probing Instruments ● Polaris Guidance and Fire Control Instruments ● Collimation Test Instruments ● Deviators ● Borescopes — Electronic and Visual

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Auto-Collimators — Electronic and Visual ● Electronic Levels ● Gravity Reference Instrument ● Jig Theodolite ● Angle Index Tables and Readout Devices ● Gratings ● Targets and Special Scales

Instruments for Manufacturing, Inspection, Quality Control

A complete line of alignment instruments and accessories

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OPTICS AND METROLOGY DIVISION

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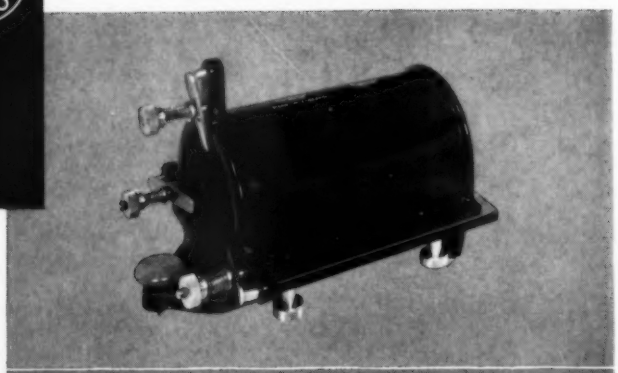
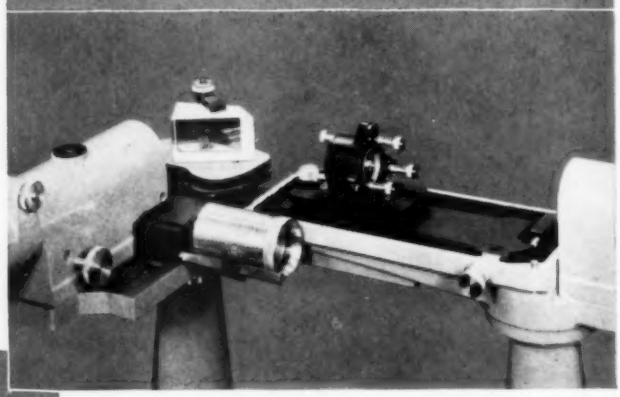
HIGH RESOLVING POWER APPARATUS

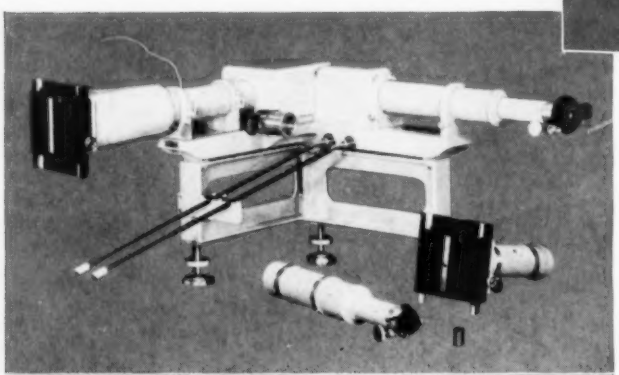
HILGER & WATTS

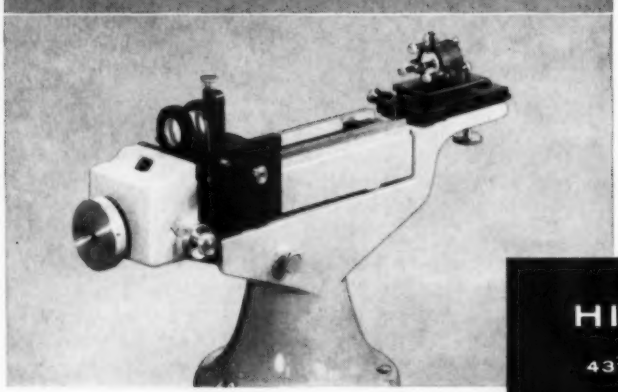




The development of the maser and laser has substantially broadened the use of high resolving power apparatus. Hilger & Watts now provide a comprehensive selection of equipment to meet the increased requirements.

Among the more important are etalon and interferometer plates — ranging from 20 mm. aperture to 100 mm. aperture; with flatnesses to 1/200 of a wavelength. Mounts for these plates, as well as wave length spectrometers designed to accommodate etalons within the instrument, are standard stock items.





Other new developments include: motor driven Fabry-Perot and Michelson interferometers with fringe counting and amplitude measuring equipment; dielectric coatings for all plates. Lummer-Gehrcke plates and transmission echelon gratings are also available.

Illustrated Top Right—
B345 100 mm. Aperture Etalon

Illustrated Center Right—
D186 Spectrometer with Etalon mounted

Illustrated Center Left—
D260 Large Aperture Spectrometer with Etalon

Illustrated Bottom Left—
N34 Interferometer with Etalon

• *Ask for individual catalog sheets and for complete instrument listing.*

HILGER & WATTS, INC.

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